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PROCESS FOR THE ECONOMICAL UTILIZATION OF IDLE STANDBY
OILGAS PLANTS TO PRODUCE LOW-COST PETROCHEMICALS

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Natural gas covering over 97% of the requirements of the U.S. gas industry(1) has almost completely replaced manufactured gas produced from coal, coke or oil, which still represents over 99% of the gas distributed in Europe (9).

In most cases, in the U.S.A., gas plants have been converted to produce oil-gas and are being maintained as standby facilities to cover peakloads, sometimes so required by State Utility Commissions. However, in general, such plants (appr. 150 gas generators), are operated for less than 15 days per year.

This situation is economically unsound, when considering the important capital investment in such plants, the required maintenance, and the necessity of having skilled labor available all year round for only a few days' operation per year.

On the other hand, natural gas contracts generally limit the quantity of natural gas available for peakloads, which may be as high as 4 times the lowest sendout volume. Price for extra peakload gas may be up to 6 times the average cost of natural gas. With the increase in space heating load, the dynamic competition of other fuels and the upward trend in the cost of natural gas, the peakload problem is becoming increasingly acute.

A solution is proposed which is believed to solve the peakload problem of the gas industry. Its application will permit continuous year round operation of presently idle gas plants.

This solution provides to produce oilgas with a higher than conventional heat value and which may contain up to 50% higher hydrocarbons (C_2 to C_8). Recovery, fractionation and further processing of such hydrocarbons would then make available basic petrochemicals. Due to the high value of petrochemicals recovered from the oilgas, the residual gas can be made available at a lower cost than that of natural gas. The residual gas is more readily interchangeable with natural gas than oilgas. During most of the year, residual gas may be used to cover heat and power requirements; during peakload periods, it can be made available for gas distribution and liquid fuels are used for the plant.

The process can make available to the chemical industry basic petrochemicals such as ethylene, propylene, butylene-butadiene, cyclopentadiene, benzene, toluene, cumene and styrene. Production would be nearer to large consumption

areas, as for instance on the East Coast of the U.S.A., and possibly at lower cost than that prevailing on the Gulf Coast.

Taking ethylene as an example: 62.6% of the total U.S. production originates from the Gulf Coast at a price of appr. 5cents/lb. and only 15.4% from the East Coast at appr. 6 cents/lb. such prices being based on plants of 200 to 300 million pounds per year capacity (8).

With this solution, it would be possible to produce ethylene at a price of appr. 2.5 cents/lb., in New England in a plant having a capacity of only 43 million pounds per year (oilgas plant of 10,000 MCFD). In this case, the residual gas is valued at 30% below the average cost of natural gas, and the other products at their market value in this area.

A plant with an annual capacity of 26 million pounds of ethylene (6,000 MCFD gas plant) would still be economically feasible with this solution, whereas such relatively small plants are not competitive when using other processes. By application of the proposed solution at a single converted gas plant in the N.Y. metropolitan area, 150 million pounds of ethylene could be obtained and this right near major markets for the products.

The growth of the petrochemical industry has been dynamic and continues at an unprecedented rate. During the last two decades, production in the U.S.A. had doubled about every five years. In 1958, it amounted to appr. 5 billion dollars annually, and is expected to grow to 20 billion dollars by 1967(6).

In papers presented at the World Petroleum Congress held recently in New York, as well as in several publications (6, 7) production of petrochemicals over a decade has been forecast as per following Table.

Anticipated Increase in Production of some Basic Petrochemicals in the United States in a Decade in Billion Pounds

	<u>1955</u>	<u>1965</u>
Ethylene	3.05	6.50
Propylene	1.60	2.70
Butylene-Butadiene	2.15	3.60
Aromatics	3.00	8.00
Styrene	1.01	1.75
All Petrochemicals	31.50	85.00

Natural gas is the principal source (50%) from which ethylene is produced in the U.S. (8). Natural gas contains relatively small percentages of ethane from which ethylene is produced by thermocracking, after recovery of ethane from natural gas. In our case, the ethylene is already present as such in the oilgas (over 20% by volume) in addition to other hydrocarbons the total content of which may be as high as 50% by volume. This allows lower capital investment and permits the economical recovery of hydrocarbons in smaller plants.

The Stark Process (U.S. Patent No. 2,714,060) proposed in this paper has been described previously in several publications (2, 3, 4, 5, 11) This process offers a great deal of flexibility regarding the degree of hydrocarbon recovery, purity and type of products which can be obtained.

A number of schemes, A to E, mostly new, have been worked out to show various possibilities in recovery and production of petrochemicals and their economics are outlined hereafter.

In all of the following schemes, oilgas is the basic charge stock for the proposed recovery and petrochemical plants. The oilgas is produced in existing converted, reactivated or new gasplant facilities.

The conventional oilgas generator permits vapor phase cracking with steam but without catalyst. A variety of fuels such as Bunker C oil, residuum crude oils, and crude oil may be used for oilgas making. The oilgas generator can be heated by heavy oil, tar or gas. By suitable adjustment of the operating conditions, particularly of the cracking temperature, an oilgas of desired analysis and heat value (700 Btu/cf to 1600 Btu/cf) can be produced. As the hydrocarbon content of the gas (C_2 to C_8) increases, the heating value of the oilgas increases accordingly. It may range between 5 mol percent for a 700 Btu/cf gas to 50 mol percent for a 1600 Btu/cf gas(10).

The present study is based on a typical oilgas of 1250 Btu/cf having the following analysis expressed in mol percent, based on operating data available from various plants.

CH ₄	33.0%	
C ₂	24.0%	
C ₃	6.6%	
C ₄	3.8%	
C ₅	1.2%	
C ₆ -C ₈	3.4%	
H ₂	16.0%	
CO, CO ₂ , O ₂ , N ₂	12.0%	Heat value 1250 Btu/cf
	100.0%	Gravity 0.86

The combined percentage of unsaturated hydrocarbons and aromatics in above analysis represents appr. 35%. The residual gas after recovery of higher hydrocarbons will have a heat value and gravity nearer to the natural gas and may be used as a substitute thereof, with better interchangeability and characteristics than the conventional oilgas of 1000 Btu/cf. The residual gas may, however, also be used within the plant itself to provide for heat and power requirements. Depending on local market conditions, by crediting the market value of the recovered petrochemicals, this may result in a lower cost for residual gas than for the price of natural gas in the specific area.

The H₂S is removed from the oil and the tar is separated and dehydrated at the gas plant by conventional procedures. The oilgas accumulated in the holder is compressed and sent to the recovery plant.

As the organic sulphur compounds generally contained in the oilgas (appr. 30 grains/100 cf) are removed from the gas during the recovery processing, the residual gas will be practically free of organic sulphur and can, if so desired, be used in a catalytic generator for the production of hydrogen, which cannot be obtained from the oil directly because of this sulphur (12). This allows also to build ammonia plants starting from heavy oil as the only charge stock. In such case, hydrogen could be produced from the residual gas and any balance of the residual gas could be used to cover the important heat and power requirements of the ammonia plant. This possibility is not covered in this paper.

Schemes A to E are outlined below:

Scheme A (Fig. 1)

This plant proposes the recovery of appr. 70% of C_3 , and more than 98% of C_4 to C_8 cuts (2). The residual gas will have the following appr. analysis in mol percent:

CH_4	38.0%
C_2	27.0%
C_3^+	2.6%
H_2	18.4%
CO, O_2, CO_2, N_2	<u>14.0%</u>
	100.0%
Heat value	970 Btu/cf
Gravity	0.68

Scheme B (Fig.2)

Recovery of 88% of the C_2 fraction and appr. 98% of the higher hydrocarbons (C_3 is proposed). The residual gas will have the following appr. analysis in mol percent:

CH_4	49.2%
C_2^+	9.1%
H_2	24.7%
CO, CO_2, O_2, N_2	<u>17.0%</u>
	100.0%
Heat value	750 Btu/cf
Gravity	0.58

The residual gas can be enriched to a gas of 1000 Btu/cf and ^{appr.} 0.70 gravity using appr. 4% of the annual output of the recovered C_3 cut.

Scheme C (Fig.3)

Provides for the addition to the recovery plant as per Scheme A of another Plant (P1) to handle 50% of the residual gas.

Part of the residual gas, with addition of benzene, is sent to Plant P1, where all of the propylene in the gas with the benzene is catalytically converted to cumene (C_9H_{12}), and the ethylene with the benzene is converted to ethylbenzene (C_8H_{10}) an aromatic solvent remaining as byproduct. The ethylbenzene can then be dehydrogenated into styrene (C_8H_8) in an additional plant P2.

The quantity of cumene and styrene produced may be varied by changing the percentage of volume of residual gas processed in plants P1 and P2.

Scheme D (Fig. 3)

Shows conditions when all of the residual gas is processed in plants P1 and P2, otherwise at the same conditions as Scheme C.

Scheme E (Fig. 4)

Refers to an alternate in which the first plant is limited to the extraction of 95% of C_4 and heavier fractions. Plants similar to D are provided, however, all of the C_3 will be used in Plant P1 resulting in greater cumene production than provided for in the preceding scheme, but no propylene cut is recovered.

A typical example is given for a plant with a daily capacity of 6,000 MCFD of oilgas corresponding to the operation of only one large size conventional oilgas generator unit.

An oilgas of 1250 Btu/cf, typical analysis as above, based on 345 days of operation per year, has been assumed; this amounts to an input in the extraction plant of 7,500 MM Btu/day or 2,587,700 MM Btu/year. Consumption of heavy oil for gas making and heating of the oilgas generator based on 15.5 gal/MCF is 764,000 bbl/year.

The following tables illustrate the economics of such typical plant for each of above schemes, based on present market conditions prevailing in the New England area.

Table I, indicates quantities produced, as well as charge stocks, on an annual basis.

Table II, shows the upgrading, i.e. market value of the product obtained less the cost of charge stocks (heavy oil and benzene) with corresponding unit prices for each product.

Residual gas has been estimated at the cost of heavy fuel in equivalent Btu, i.e. 35¢/MMBtu, plus 10% for difference in efficiency and cost of preheating of the heavy oil making a total of 38.5¢/MMBtu. This is 30% lower than the average cost of natural gas in the New England region (appr. 55¢/MMBtu). It makes possible to use residual gas as fuel, either partially or totally, for petrochemical or power plants or gas distribution. Above calculations do not reflect credit for the much higher value of residual gas when used for peakload requirements (other substitutes being up to 6 times higher)

An economic evaluation for each scheme is summarized in Table III.

The required capital investments should be established separately for each project, however, an indication has been given in Tabulation III.

Equity has been assumed at 50% of the capital requirements, interest rate at 6 percent per annum on balance of required capital with amortization over 10 years resulting in an average annuity of 3.59%

Cost of utilities and labor on which these studies are based:

Steam	70¢/1000 lbs.
Electricity	1.1¢/KWH
Fuel oil	\$2.20/Bbl
Fuel gas	38.5¢/MCF
Water	0.5¢/1000 gals
Skilled labor	\$2.40/hour

A conservative figure of 20¢ per MCF has been used for the cost of oil-gas at holder including tar dehydration.

The return on total capital is defined as income plus interest divided by the total capital.

The payout is defined as number of years resulting from the capital investment divided by net income after taxes plus depreciation.

Tabulation III shows that the net return on capital equity after taxes is 21% to 72% and payout 4.7% to 2.1 years based on above conditions.

Figs. 5 and 6 illustrate payout and percentage of net income after taxes on the equity (50% of capital) for Schemes A thru E above, for plants of capacities from 3,000 MCFD to 10,000 MCFD based on present market conditions in the New England area.

A specific study should be made for each case as the economics will depend on the local and market conditions.

If payout of 5 years is taken as a basis for Scheme B and for a plant of 10,000 MCFD capacity, the cost of ethylene for a production of 43 million pounds per year (instead of 26 million pounds/year in a 6,000 MCFD plant) may be as low as 2.5¢/lb in the New England area.

The cost of styrene under above conditions for a plant of 10,000 MCFD, using this process will be only appr. 8¢/lb. and of cumene 5.3¢/lb. i.e. appr. 30% lower than market prices in the New England area.

It is to be emphasized that, depending on market conditions, plants of smaller capacity become economically feasible by application of this process. This may be of special importance for plants outside the United States where smaller quantities of petrochemicals are marketable and can be produced at much lower cost than they can be imported.

The application of this process will result in the following advantages:

- 1) Utilization of idle investment in gas plants by operating them all year round, instead on only less than two weeks a year.
- 2) Possibility of making available to the gas industry a better substitute gas at much lower cost than other substitutes for peakloads and appr. 30% lower than the average yearly cost of natural gas in the area.
- 3) Possibility of making available to the chemical industry basic petrochemicals closer to the consuming markets (for instance the East of the U.S.) at a price possibly lower than prevailing on the Gulf Coast of U.S.A.
- 4) To obtain a high net income on equity capital after taxes (21% to 72%) and payout of the investment in 2 - 5 years.
- 5) Possibility to install plants of small capacity which is, in general, not economically possible with other processes.

- 6) Economic utilization of heavy oils, either Bunker C oil or crude oil, which may be either in oversupply or too far from market areas.

This process may show even better economics when applied in other countries even if installation of gas plant equipment may be required, because chemicals are generally imported and their cost is higher than in U.S.A whereas labor is less expensive.

Application of this process may benefit both the gas and chemical industries and may contribute to better standards of living in many countries.

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TABLE I

PRODUCTS AND REQUIRED CHARGE STOCKS

FOR DIFFERENT SCHEMES FOR A TYPICAL 6000 MCF/D PLANT

	A	B	C	D	E
<u>PRODUCTS</u>					
Residual Gas	1,675,000	1,020,000	1,280,000	950,000	970,000
Tar	MM BTU /yr MM gals/yr	14.10	14.10	14.10	14.10
Ethylene	MM lbs /yr	26.30			
Propylene Cut	MM gals/yr	3.85	2.83	2.83	2.23
Butadiene-Butylenes Cut	MM gals/yr	2.23	2.23	2.23	.67
Cyclopentadiene-Pentene Cut	MM gals/yr	.67	.67	.67	2.16
BTX (Benzene-Toluene-Xylene)	MM gals/yr	2.16	2.16	2.16	84.50
Styrene	MM lbs /yr		41.90	83.80	38.20
Cumene	MM lbs /yr		5.04	10.04	
Aromatic Solvent	MM gals/yr		.82		

CHARGE STOCKS

Heavy oil for oil-gas making and heating					
oil-gas generator		.764	.764	.764	.764
Benzene	MM bbl /yr			11.500	14.100
Alternate	MM gals/yr				
Benzene required, if Benzene from BTX is used			4.320	10.070	12.670

TABLE II

UPGRADING VALUES IN MILLION DOLLARS/YEAR FOR DIFFERENT
SCHEMES FOR A TYPICAL 6000 MCF/D PLANT WITH UNIT PRICES OF PRODUCTS

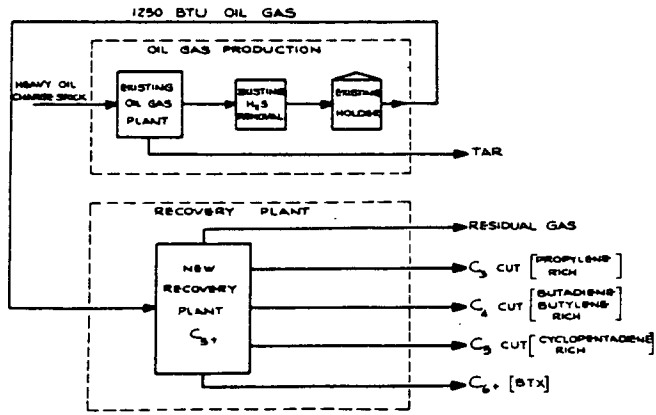
	Unit Prices				
	A	B	C	D	E
<u>VALUE OF PRODUCTS</u>					
Residual Gas	.645	.392	.492	.366	.373
Tar	1.410	1.410	1.410	1.410	1.410
Ethylene	.05 /lb	1.313			
Propylene	.14 /gal	.539	.396	.396	
Butadiene-Butylenes	.09 /gal	.200	.200	.200	.200
Cyclopentadiene-Pentenenes	.09 /gal	.060	.060	.060	.060
BTX	.389	.389	.389	.389	.389
Styrene	.18 /gal		5.020	10.040	10.120
Cumene	.12 /lb		.403	.806	3.060
Aromatic Solvent	.08 /lb		.123	.246	.308
	.15 /gal				
TOTAL	3.100	4.303	8.493	13.913	15.920
<u>COST OF CHARGE STOCKS</u>					
Heavy oil for oil-gas making and heating oil-gas generator	1.680	1.680	1.680	1.680	1.680
Benzene			1.780	3.560	4.360
TOTAL	1.680	1.680	3.460	5.240	6.040
<u>UPGRADING VALUES</u> (Equal to Value of Products less Cost of Charge Stocks)	1.420	2.623	5.033	8.673	9.880

TABLE III

ECONOMIC EVALUATION OF DIFFERENT SCHEMES

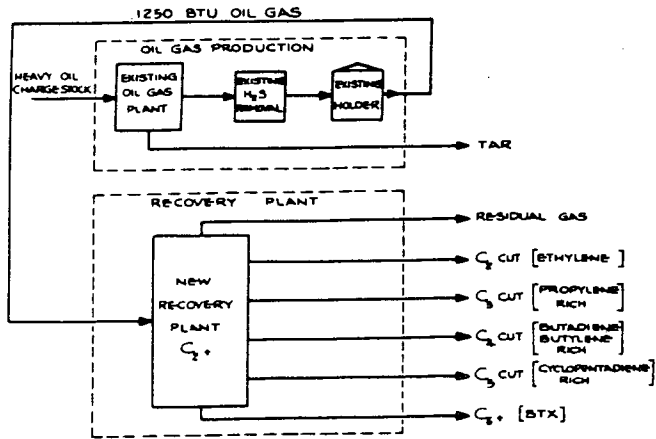
IN MILLION DOLLARS/YEAR FOR A TYPICAL 6000 MCF/D PLANT

	A	B	C	D	E
Estimated Capital Investment	2.10	3.90	6.10	8.20	7.90
Financing, Equity (50%)	1.05	1.95	3.05	4.10	3.85
Loan	1.05	1.95	3.05	4.10	3.85
COSTS, MM \$/yr					
Gas Manufacturing Plant					
incl. tar processing,	.416	.416	.416	.416	.416
but excl. charge stock					
Petrochemical Plant	.097	.234	.878	1.659	1.720
Utilities and Chemicals	.080	.193	.216	.216	.193
Labor					
Miscellaneous					
incl. maint., insur., gen.	.135	.263	.568	.870	.914
man., sales, royalties etc.	.193	.375	.571	.764	.727
Depreciation (10 yrs)					
Interest, 6% amort. 10 yrs.	.038	.070	.110	.147	.138
(average 3.59% per year)					
TOTAL.	.959	1.551	2.759	4.072	4.108
Upgrading (Value of Products, less					
Costs of Charge Stock)	1.420	2.623	5.033	8.673	9.880
Income	.461	1.072	2.274	4.601	5.772
Income Taxes (52%)	.240	.556	1.182	2.395	3.000
Net Income	.221	.516	1.092	2.206	2.772
% Return on Equity after Taxes	21.0	26.5	35.8	53.8	72.0
% Return on Capital Investment after Taxes	12.3	15.0	19.7	28.7	36.9
Payout after Taxes	4.7	4.2	3.4	2.6	2.1



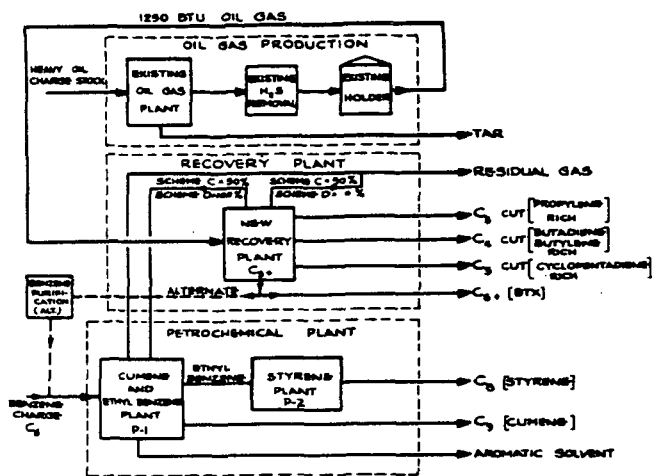
SCHEME A

FIG. I



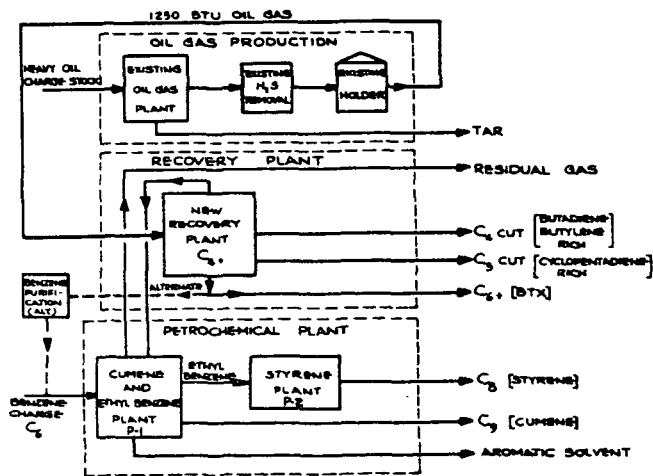
SCHEME B

FIG. II



SCHEMES C AND D

FIG III



SCHEME E

FIG IV

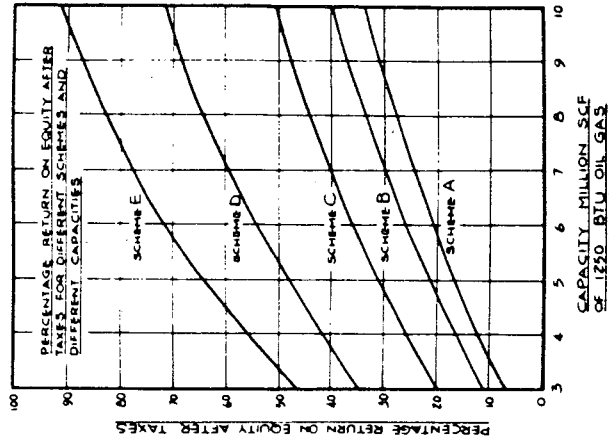


FIG VI

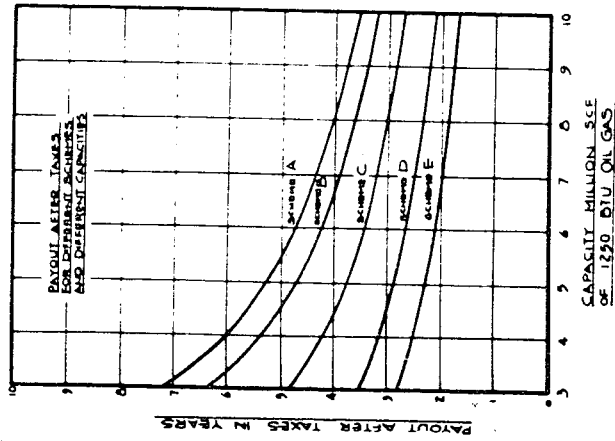


FIG V

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Hydrogenation of Coals and Chars to Gaseous Hydrocarbons

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INTRODUCTION

The hydrogenation of coal is being considered in this country and abroad for production of high B.t.u. gas for meeting peak-load demands of the gas industry and as a method for augmenting future supplies of natural gas. Experiments on the hydrogenation of coal and chars to gaseous products have been investigated by Dent,¹ Channabasappa,¹ and the Bureau of Mines² at 500 to 3000 pounds per square inch gauge, 500 to 750°C., with very long residence times. Recently the Bureau of Mines extended these studies⁴ to 6000 pounds per square inch gauge and 800°C. with a coal from Rock Springs, Wyoming, using very short residence times. This paper discusses the amenability of other coals and chars to conversion to gaseous hydrocarbons at 6000 pounds per square inch gauge and 800°C.

EXPERIMENTAL PROCEDURE

A flow sheet of the apparatus is shown in figure 1. Hydrogen flowed from a storage vessel into the bottom of the reactor through a preheat zone and into the bed of coal or char. After a constant flow of hydrogen was established, the reactants were heated to 800°C. in 1-1/2 minutes by passing a high current through the tube at points E and E₁. Hydrocarbon vapors and gases and excess hydrogen passed at pressure into a small condenser-receiver where the bulk of the oils were collected in a small glass vial. Noncondensable gases were reduced to atmospheric pressure, passed into a small gasholder, and after an appropriate storage period they were sampled, metered, and finally vented. At the end of an experiment, the reactor and its charge were cooled to room temperature by spraying with cold water. After the bulk of the unreacted solids were removed, the reactor was washed with benzene to remove the remainder of solids and high molecular weight oils. The unreacted solids and benzene washings were filtered and the solids were extracted with benzene in a Soxhlet apparatus. The percentage of coal reacted was then calculated by subtracting the weight percent of unreacted organic solids (organic benzene insolubles) from 100. The filtrate and extract were not analyzed.

Oils which were collected in the condenser-receiver were analyzed semi-quantitatively in a mass spectrometer using a low ionizing voltage technique. Gaseous hydrocarbons in the effluent gas stream were also analyzed by the mass spectrometer.

Yields of oils and hydrocarbon gases were expressed as weight percentages based on moisture- and ash-free coal or char. Total yields on this basis would be larger than 100 by an amount equal to the percentage of hydrogen absorbed based on moisture- and ash-free coal or char.

Studies were made with high-volatile bituminous coals from Pittsburgh, Pennsylvania and Rock Springs, Wyoming, a lignite from Rockdale, Texas, a medium-volatile anthracite from Luzerne County, Pennsylvania, and a char from Rock Springs, Wyoming coal. The char was prepared by heating the coal in helium for 2 hours at 600° C.; it represents the type of material which could be produced commercially by carbonization at low temperatures. Ultimate analyses of the substrates are shown in table 1. The coals and char were all pulverized and screened to 30 x 60 mesh. Ammonium molybdate was added² to a weight of water 1.3 times the weight of coal or char to provide 1 percent molybdenum on the substrate. After standing for 5 minutes, the solution was added to the substrate and concentrated by evaporating on a hot plate with constant stirring at 100°C. The mixture was finally dried on a tray in air at 70° C. for 20 hours.

Experiments were conducted at 6000 pounds per square inch gauge and 800° C. and residence times of zero to 15 minutes. Zero residence time is defined as the time at which the coal attains reaction temperature. Flow of hydrogen was 100 standard cubic feet per hour, corresponding to a nominal linear velocity at pressure and temperature of 0.5 foot per second. In all cases, this rate of flow was sufficient to absorb the heat of reaction and thus maintain adequate control of temperatures.

RESULTS

Conversions of coal and char to gases and liquids are shown in figure 2. Bituminous coal and lignite were more readily hydrogenated than the char and anthracite. This observation is reasonable because of the less condensed structures of lower rank coals. Increase in residence time from "0" to 15 minutes resulted in an increase in conversion for Texas lignite from 90 to 97 percent, based on moisture- and ash-free feed, and an increase in conversion with the bituminous coals from 75 to about 90 percent. Although conversions for char and anthracite were low at "0" time, they increased to 67 and 53 percent, respectively, during the first three minutes and at the end of 15 minutes the conversion of char and anthracite amounted to 84 and 65 percent, respectively.

The carbonaceous residues remaining in the reactor from bituminous coals and lignite were agglomerated, whereas, residues from char and anthracite were free-flowing. Agglomeration was less severe with Texas lignite than with bituminous coals.

Yields of oil from bituminous coals and lignite were independent of residence time. Virtually no oils were produced from char or anthracite. As shown in figure 3, yields from Texas lignite, Rock Springs, Wyoming and Pittsburgh coals were 32, 26, and 20 percent, based on moisture- and ash-free coal, respectively. As yields of oil

did not increase with increase in retention time, it appears that the bulk of the oils were formed during heating to 800° C. Past experiments have shown that the formation of oil begins at about 400° C., increases rapidly as the coal is heated to 525° C., and from there on decreases because of cracking reactions.

About 90 percent of the oil was collected as overhead material in the condenser-receiver, the remainder condensed in the connecting piping between the reactor and the receiver. Overhead oils produced from bituminous coals and lignite boiled below 300° C. and contained less than 4 percent asphaltenes. Table 2 shows the various compounds in the overhead product which were identified by mass spectrometer. It is believed that oils produced from Pittsburgh coal contained the highest quantity of alkyl benzenes and naphthalene.

Yields of gaseous products as a function of residence time are shown in figure 4. The highest yields of gases were obtained with char, followed by anthracite, Pittsburgh-seam coal, Rock Springs, Wyoming, coal, and Texas lignite. The yield of gaseous hydrocarbons at the end of 15 minutes from char was about 94 percent and the yield from Texas lignite or Rock Springs coal was about 67 to 70 percent, based on moisture- and ash-free feed. In all cases, the formation of gaseous hydrocarbons increased very rapidly during the first three minutes, and from there on the rate was smaller and approximately constant.

Methane in the gaseous products increased and C₂ and C₃ hydrocarbons decreased with increasing rank or carbon content of the substrates. Composition of gaseous products did not vary with residence time. Average compositions of the gases are shown below:

	Composition, volume-percent			Heating value, B.t.u.'s per standard cubic foot of hydrocarbons
	C ₁	C ₂	C ₃	
Texas lignite	82	15	3	1170
Wyoming coal	88	10	2	1110
Pittsburgh coal	90	9	1	1085
Anthracite	92	7	1	1090
Char	92	8	-	1045

As the flow of hydrogen was high in these experiments, the concentration of hydrocarbon gases in the effluent stream was only 2 to 4 percent. If coal was hydrogenated in a continuous unit at high partial pressures of hydrogen, the effluent gases would be recycled and the gaseous products could be removed by scrubbing with an appropriate solvent. As some hydrogen would also be removed by scrubbing, it would probably be necessary to use a low-temperature fractionation system to enrich the product sufficiently to meet specifications for commercial fuels. In this apparatus, product distribution is affected by retention time of the volatile products as well as pressure, temperature, and residence time of the coal. The effect of increasing retention time of volatiles from 6 to 30 seconds by reducing flow of hydrogen from 100 standard cubic foot per hour to 20 standard cubic foot per hour is shown in figure 5

for Rock Springs, Wyoming coal. Increase in retention time of volatiles resulted in a significant increase in yield of gaseous products and a very substantial decrease in yields of liquid hydrocarbons. For example, an increase in retention time of the volatiles from 6 to 30 seconds resulted in increasing the yield of gaseous products from 70 to 82 percent and in decreasing the yield of oil from 26 to 4-1/2 percent, based on moisture- and ash-free coal. In addition, the oil was transformed from a relatively high molecular weight product to a low-boiling material very high in benzene and naphthalene. Similar results would probably be obtained with other ranks of coal. Further increase in retention time of volatiles would probably result in production of only gaseous hydrocarbons from coal.

It was not possible to hydrogenate char or anthracite at 800° C. and 6000 pounds per square inch gauge at the lower (20 standard cubic feet per hour) flow rates of hydrogen because of uncontrolled temperatures. Under these conditions, temperatures increased to over 1000° C. and as a result, the reactor ruptured. Uncontrolled temperatures did not occur with bituminous coals and lignite under identical conditions. This overheating may be related to the type of reactions which took place. It is believed that coal, when heated rapidly to 800° C., first undergoes thermal decomposition with simultaneous hydrogenation of reactive fragments to produce oil, gaseous hydrocarbons, and a carbonaceous residue. As temperatures increase, thermal cracking of oils takes place with production of additional hydrocarbon gases and residue. Residues remaining at 800° C. are then slowly hydrogenated to gaseous hydrocarbons. Reactions are much different with char or anthracite, as only hydrogenation to gaseous hydrocarbons occurs. Thus, reactions with bituminous coals or lignite are partly endothermic and exothermic, whereas, all of the reactions with char or anthracite are exothermic. With char or anthracite, the rate of heat release is sufficiently high to cause overheating. When char was mixed with equal weights of asphaltenes or heavy oil, overheating did not occur. In this case, endothermic reactions associated with thermal decomposition of these high molecular weight materials probably absorbed sufficient heat from the exothermic reactions to prevent overheating. Overheating with char or anthracite at the lower flow rates (20 standard cubic feet per hour) of hydrogen could also be prevented by dispersing the materials in a bed of sand. No overheating occurred with char or anthracite at high flow rates (100 standard cubic feet per hour) of hydrogen. It is of interest to point out that a natural graphite from Madagascar did not react at 800° C. and 6000 pounds per square inch gauge.

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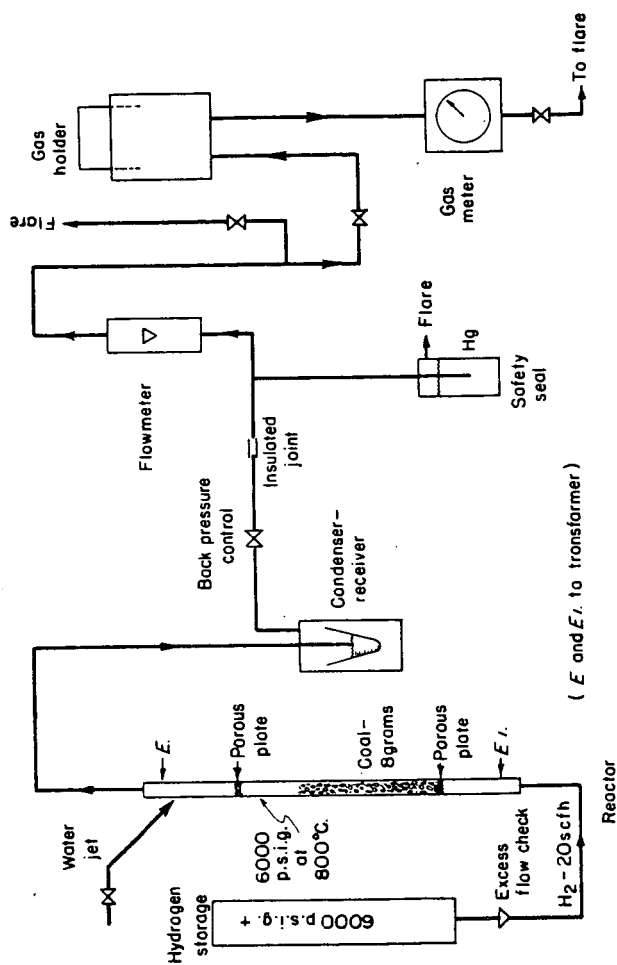
Table 1. Ultimate analyses of substrates

	<u>Moisture</u>	<u>Ash</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>	<u>Sulfur</u>	<u>Oxygen*</u>
	As received, percent						
Texas lignite	2.3	17.4	54.8	4.4	1.2	1.9	18.0
Wyoming coal	0.6	1.9	75.1	5.4	1.8	0.7	14.5
Pittsburgh coal	0.6	8.6	73.9	5.0	1.7	1.5	8.7
Anthracite	0.1	9.3	83.6	2.4	0.3	0.9	3.4
Wyoming char	0.6	2.9	87.9	2.2	1.9	0.6	3.9
	Moisture- and ash-free, percent						
Texas lignite			68.2	5.5	1.5	2.4	22.4
Wyoming coal			77.0	5.5	1.8	0.8	14.9
Pittsburgh coal			81.4	5.5	1.9	1.6	9.6
Anthracite			92.3	2.6	0.3	1.0	3.8
Wyoming char			91.1	2.3	2.0	0.6	4.0

* By difference.

Table 2. Analyses of Overhead Oils

<u>Compound type</u>	<u>Molecular weight</u>
Alkyl benzenes	78-190
Phenylnaphthalenes	204-288
Phenols	94-164
Phenanthrenes-Anthracenes	178-290
Fluorenes	166-278
Acenaphthenes-Biphenyls	154-238
Benzopyrenes-Perylenes	252-294
Naphthalenes	128-240
Binaphthyls	254-296
Indenes	116-130
Naphthols	144-214
Chrysenes	228-298
Indans	118-188
Pyrenes	202-300



L-4752

Figure 1.-Semi-continuous unit for the hydrogenation of dry coal.

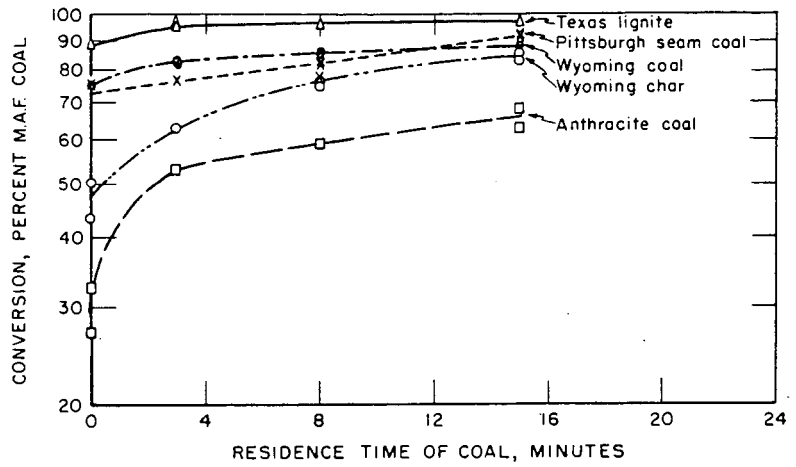


Figure 2. - Effect of residence time on conversion.

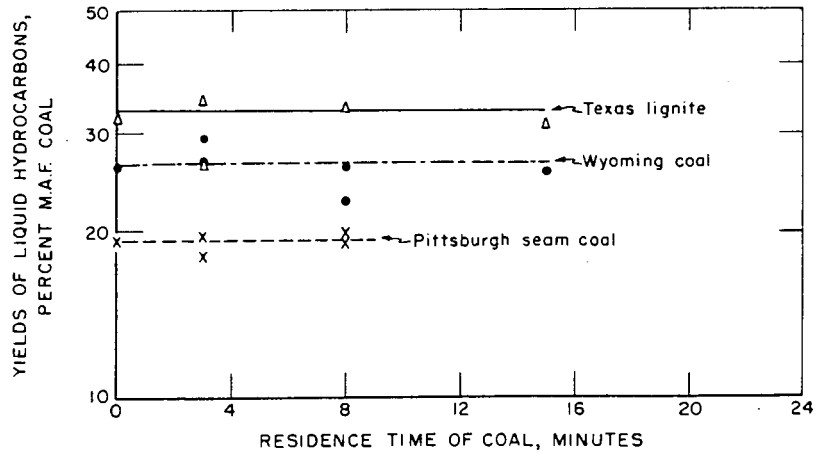


Figure 3.- Effect of residence time on yield of liquid hydrocarbons.

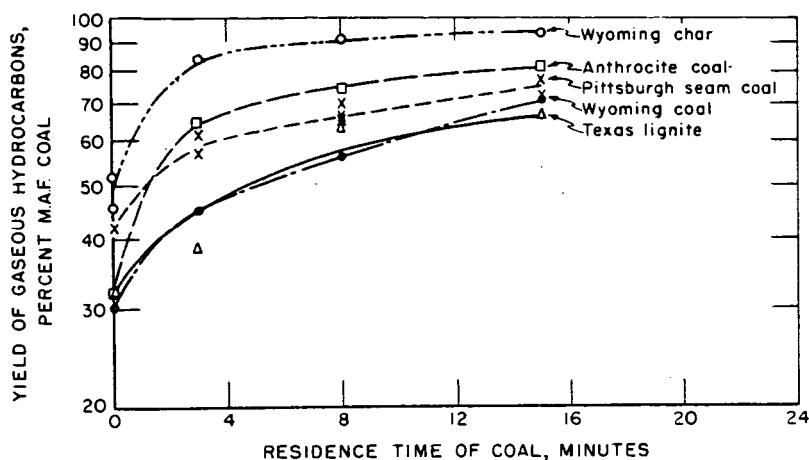


Figure 4. - Effect of residence time on yield of gaseous hydrocarbons.

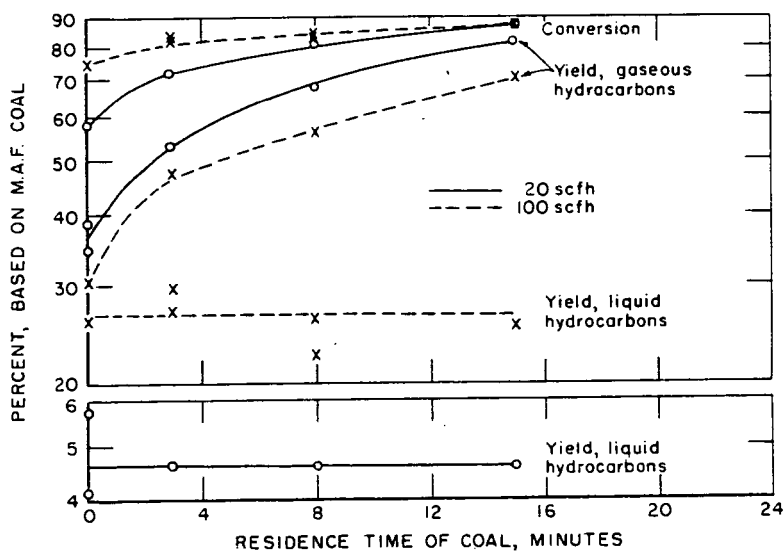


Figure 5. - Effect of residence time on product distribution for Wyoming coal at two gas rates.

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PRODUCTION OF NATURAL GAS SUBSTITUTES BY CONTINUOUS
PRESSURE HYDROGENOLYSIS OF PETROLEUM OILS

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High-pressure hydrogasification is a vapor-phase, thermal hydrogenolysis process for nearly complete conversion of distillate, crude and residual petroleum oils to fuel gases of high methane content. The required hydrogen supply may be generated by catalytic steam reforming of a portion of the product gas,^{5,10} or by partial oxidation of fresh or byproduct oil streams.⁴

Studies by Dent and others^{1,3,6} of the effects of operating variables and feedstock properties on the yield and composition of products of high-pressure hydrogasification have been directed primarily to the development of a process for producing gases of 500-600 B.t.u./SCF (SCF refers to standard cubic feet measured at 60°F., 30 inches of mercury absolute pressure, and saturated with water vapor). Work done at the Institute of Gas Technology^{11,13} has been in the range of operating conditions suitable for production of high-heating-value natural gas substitutes.

Gases of about 900 B.t.u./SCF are best produced at hydrogen to oil feed ratios corresponding approximately to the stoichiometric requirements for methane formation. Lower feed ratios result in excessive liquid products formation and carbon deposition, and higher feed ratios result in excessive hydrogen dilution. High-heating-value gas production is also favored by high pressures and long residence times. Typical operating conditions for a flow reactor are 1400°F. maximum temperature, 1500 p.s.i.g., and residence times ranging from about 100 seconds for paraffinic oils to several hundred seconds for the less reactive, higher C/H weight ratio oils; under these conditions, only about 10 wt. % of the feedstock is converted to liquid products consisting of low-boiling aromatic hydrocarbons. In low-heating-value gas production, substantially lower pressures and residence times, and higher temperatures and hydrogen feed ratios, can be employed.³

The major problem in operation of high-pressure hydrogasification processes is control of carbon deposition. The two continuous processes currently being developed for fluid feedstocks use different methods of overcoming the normal carbon-forming tendencies of crude and residual oils during hydrogenolysis. The British Gas Council^{1,3,6} has used a fluidized coke bed reactor to handle carbon laydown of somewhat less than one-half of the Conradson carbon residue of the feedstock. In the work described here, crude or residual oils were first subjected to a pretreatment step essentially equivalent to many of the hydrocracking processes now under development.^{2,8,15} Pretreatment over commercial cobalt molybdate hydrogenation catalyst at 850°F. and 1500 p.s.i.g., converted these feeds to products with either negligible or greatly reduced Conradson carbon residue, and with substantially lower C/H weight ratio. When complete conversion into a distillate product was not possible, the higher-boiling fractions containing the carbon-forming constituents were separated before charging to the hydrogasification reactor.

APPARATUS AND PROCEDURE

The apparatus comprised hydrogen and oil feed systems, prehydrogenation and hydrogasification reactors, product liquid recovery sections and a product gas metering system. A flow sheet has been presented in a preliminary study.¹³

Hydrogen was fed from storage cylinders, replenished at intervals by compression of commercial-grade cylinder hydrogen. Oil was fed from a weigh vessel through a reciprocating proportioning pump. In all runs, oil and hydrogen were mixed and introduced at room temperature.

The downflow prehydrogenator for crude and residual oil pretreatment was constructed of Type 316 stainless steel. It was 5-3/4 inches in outside diameter, 3 inches in inside diameter, and 40 inches in inside length, and was equipped at both ends with Autoclave Engineers self-sealing closures. A thermowell, 3/8 inch in outside diameter, extended concentrically into the reactor. In some runs, the prehydrogenator inside diameter was reduced to 2 inches by insertion of a stainless steel sleeve, 35 inches in length.

When the full volume of the prehydrogenator was employed, the reactants were passed through a 19-inch preheat zone of 3/8-inch diameter periclase spheres before entering the 16-inch catalyst bed, composed of equal volumes of 1/8-inch tablets of a commercial cobalt molybdate on alumina catalyst and 1/8-inch fused alumina pellets, randomly mixed. When the sleeve was used, a 20-inch catalyst bed composed of undiluted 1/8-inch cobalt molybdate tablets was located in the center of the reactor above a 9-inch zone filled with 3/8-inch diameter periclase spheres. The reported feed oil space velocity for diluted catalyst was based on the sum of the volumes of catalyst and fused alumina charged (0.0353 cu.ft. each); for undiluted catalyst, it was based on a catalyst charge volume of 0.0353 cu.ft.

The downflow hydrogasifier was constructed of 19-9DL alloy. It was 6 inches in outside diameter, 3 inches in inside diameter, and 35 inches in inside length. A 3/8-inch diameter thermowell extended into the reaction zone. The vessel was equipped at the top with an Autoclave Engineers self-sealing closure; the bottom consisted of an integral water-cooled tailpiece, which was sealed with a simple gasketed closure. In some of the tests, a sleeve similar to the one used in the prehydrogenator was inserted to reduce the inside diameter to 2 inches. For both the prehydrogenator and hydrogasifier, high-pressure condenser-separators were provided, from which gases were continuously recovered and liquids intermittently removed.

A 100 cu.ft./hr. wet-test meter was used to measure product gas flow rates. A proportional sample of product gas was collected in a water-sealed holder for analysis.

Reactor temperatures were sensed by Chromel-Alumel thermocouples, and pressures by Bourdon tube gages. Temperatures were measured and recorded by means of a potentiometer strip-chart; reactor and orifice pressures were also recorded.

In initial tests, the prehydrogenator and hydrogasifier were operated simultaneously, with the entire effluent from the prehydrogenation step passing to the hydrogasifier. However, the periods of adequate catalyst performance at the high temperatures required for complete removal of carbon-forming materials from residual and low-grade crude oils were limited by catalyst carbon deposition. Consequently, it appeared more practical to operate the prehydrogenator at less severe conditions, and to separate any high-boiling, asphaltene-containing materials from the hydrogasifier feed. This was simulated by pre-

hydrogenation, distillation of the liquid products, and hydrogasification of the 0°-360°C. fraction. The hydrogen to oil feed ratio to the hydrogasifier was adjusted to account for the hydrogen consumed in prehydrogenation.

Product gases, and 0°-160°C. fractions of product liquids, were analyzed with a Consolidated Engineering Co. Model 21-103 mass spectrometer. Other analyses were conducted in accordance with standard ASTM methods, with the following exceptions: prehydrogenator product liquid 500-gram distillations were carried out at atmospheric pressure using a procedure similar to ASTM Method D1160-56T;¹⁴ carbon and hydrogen ultimate analyses were made by combustion train, with the Grace and Gauger modification⁷ of ASTM Method D271-44.

Specific gravities and ideal gas heating values were calculated from gas analyses. Feed and product gas volumes and heating values were calculated at conditions of 60°F., 30 inches of 32°F. mercury absolute pressure, saturated with water vapor. Specific gravities were computed from the average molecular weight of the dry gas, and were based on air of molecular weight 28.97.

PROCESS CHARACTERISTICS

Selected prehydrogenation and hydrogasification results for typical feedstocks are shown in Tables 1-3 to illustrate the characteristics of the process under the preferred operating conditions. The premium feedstocks, kerosine and diesel oil, required no pre-treatment before hydrogasification. The properties of Aruba reduced crude were sufficiently improved by prehydrogenation to permit use of the total product oil as hydrogasification charge stock. The relatively low-grade Taparito crude oil still had a substantial Conradson carbon residue after prehydrogenation, so that only the 0°-360°C. distillate fraction was used as hydrogasification charge stock. Recycle of the residue fraction to effect further conversion to distillate was found to be practical. Prehydrogenation results for Boscan crude oil are also shown to illustrate that, after fractionation, an acceptable hydrogasification charging stock could be obtained from a crude oil feedstock typical of the lowest grade suitable for the process. The prehydrogenation conditions used in obtaining the data of Table 2 were determined to give practical on-stream periods of the commercial catalyst used.

Table 3 shows the hydrogasification results of the distillate and prehydrogenated oils at about 1400°F. maximum reaction temperature and hydrogen to oil feed ratios corresponding to the stoichiometric requirements for methane formation. The distillate oils, and the 0°-360°C. fraction of the prehydrogenated Taparito crude oil, did not give carbon deposition in the hydrogasifier; the prehydrogenated Aruba reduced crude charge, which had a Conradson carbon residue of 0.41 wt. %, did give a small carbon deposit. This suggests that even small amounts of objectionable high-boiling fractions in the prehydrogenated oil should be removed to ensure carbon-free hydrogasifier operation.

Because of the high reactivity associated with its low C/H weight ratio, kerosine gave results comparable to those of the other feedstocks at considerably less severe conditions; kerosine produced approximately 900 B.t.u./SCF gas of high methane-plus-ethane content at 500 p.s.i.g. and approximately 50 seconds residence time, whereas the other feedstocks required a pressure of 1500 p.s.i.g. at a residence time of approximately 300 seconds. The relatively high ethane content of the product gas from kerosine is typical of operation at comparatively short residence times with paraffinic (low C/H weight ratio) charging

Table 1.-PROPERTIES OF DISTILLATE OIL FEEDSTOCKS

Feed oil designation	Kerosine	Diesel Oil
Specific gravity 60°F./60°F.	0.805	0.838
°API	44.2	37.3
Viscosity, centistokes at 100°F.	n.d.	2.862
Ultimate analysis, wt. %		
Carbon	85.88	86.27
Hydrogen	14.05	13.50
Sulfur	0.04	0.30
Ash	n.d.	0.000
Carbon/hydrogen wt. ratio	6.11	6.39
Distillation (ASTM D158-41), °F.		
Initial boiling point	349	382
10%	384	452
20%	396	470
30%	406	486
40%	413	497
50%	421	507
60%	429	520
70%	439	536
80%	450	554
90%	470	580
End point	518	639
Distillation residue and loss, ^a %	2	2
Heat of combustion, B.t.u./lb. ^a	19960	19730

^aEstimated from Reference 9.

Table 2.-PREHYDROGENATION OF CRUDE AND RESIDUAL OILS

Feed oil designation Run No.	Aruba Reduced Crude 71	Tapiato Crude 80	Roscan Crude 100
Prehydrogenation conditions			
Maximum temp., °F.	850	850	845
Average catalyst bed temp., °F.	835	825	810
Pressure, p.s.i.g.	1500	1500	1500
Feed ratio, SCF H ₂ /lb. cu.ft. oil/cu.ft. catalyst bed-hr.	31.59	32.96	31.98
Prehydrogenator off-gas composition, mole %	0.87 ^a	0.42 ^b	0.42 ^b
Wt. % of carbon in feed	5.8	4.6	5.0
N ₂ + CO + CO ₂	0.5	0.4	0.3
H ₂	97.2	97.7	97.7
CH ₄	1.1	0.7	0.9
Higher paraffins	1.0	1.0	1.0
Olefins	0.2	0.2	0.1
Total	100.6	100.6	100.6
Catalyst carbon, wt. % of carbon in feed	n.d.	0.86	0.94
Oil properties			
Specific gravity	0.951	0.888	0.894
60°F./60°F.	21.5	17.8	26.7
API	203	66.0 ^e	95.5
Viscosity, S.S.U. at 122°F.	84.88	85.55	86.39
Ultimate analysis, wt. %			
Carbon	11.72	12.02	12.57
Hydrogen	1.62	1.01	1.58
Sulfur	0.05	0.03	0.08
Ash	7.24	7.13 ^f	6.98
Carbon/hydrogen wt. ratio	7.4	4.5	5.0
Conradson carbon residue, wt. %			
Distillation, wt. %			
0°-160°C.	1.1	2.7	1.7
160°-200°C.	1.1	2.4	2.1
200°-300°C.	25.5	25.0	22.0
300°C.-end point	12.3	13.0	11.8
Residue and loss	60.0	46.8	51.6
End point, °C.	335	341 ^g	333 ^g
Heat of combustion, B.t.u./lb. h	19120	19200	19290

^a Catalyst bed consisted of 0.0353 cu.ft. undiluted cobalt molybdate catalyst.
^b Catalyst bed consisted of 0.0353 cu.ft. cobalt molybdate and 0.0353 cu.ft. fused alumina pellets, randomly mixed.
^c Feedstock for hydrogasification Run No. 72.
^d Feedstock for hydrogasification Run No. 89 - composite of 0°-360°C. fractions of product oils from four prehydrogenation tests at 850°F.
^e S.S.U. at 122°F.
^f Calculated from value for residue fraction.
^g Obtained at 400°C. pot temperature.
^h Estimated from Reference 9.

Table 3.-HYDROGASIFICATION OF DISTILLATE OILS AND
PREHYDROGENATED CRUDE AND RESIDUAL OILS

Feed oil designation	Kerosine	Diesel Oil	Total Prehydrogenated Aruba Reduced Crude	0°-360°C. Fraction of Prehydrogenated Taperito Crude
Run No.	62A	33-C	72	89
Oil rate, lb. C/hr.	3.06	1.50	1.51	1.50
Hydrogen feed ratio % of stoichiometric ^a	98.0	99.9	99.5	100.3
SCF/lb.	27.67	29.51	31.13	30.54
Pressure, p.s.i.g.	500	1500	1500	1500
Temperature, °F.				
Average ^b	1325	1335	1355	1305 ^c
Maximum	1400	1395	1405	1395
Residence time, sec. ^d	51.0	301	304	319
Hydrogen consumption, SCF/lb.	16.2	22.3	23.9	22.6
Product recovery, wt. % of oil + hydrogen fed	103.5	101.7	99.0	97.2
Product distribution, %				
Gas	88.9	93.2	91.1	91.0
Liquid	11.1	6.8	8.7	9.0
Carbon	nil	nil	0.2	nil
Product gas yield, SCF/lb.	29.58	30.19	29.20	29.28
SCF/cu.ft. reactor-hr.	726.9	362.8	353.1	354.2
Net thermal recovery, % ^e	90.4	88.9	80.1	80.1
Product gas properties				
Composition, mole %				
N ₂ + CO + CO ₂	0.8	0.4	1.2	0.4
H ₂	38.8	23.8	24.7	27.2
CH ₄	40.5	69.7	69.7	66.2
C ₂ H ₆	17.1	5.3	3.4	5.4
C ₃ H ₈	0.4	--	--	0.1
i-Butane	0.1	--	--	--
Olefins	1.0	0.1	--	--
Benzene	1.2	0.7	1.0	0.7
Toluene	0.1	--	--	--
Total	100.0	100.0	100.0	100.0
Heating value, B.t.u./SCF	909	893	872	868
Specific gravity (air = 1)	0.495	0.482	0.478	0.466

^aStoichiometric for complete conversion of C + H in feed oil to methane.

^bBased on average of temperatures measured at centers of three equal zones.

^cInterpolated value.

^dBased on dry product gas volume at reactor pressure and average temperature.

^e
$$\frac{\text{Heat of combustion of product gas} - \text{heat of combustion of feed hydrogen}}{\text{heat of combustion of feed oil}} \times 100.$$

stocks. The conditions employed for diesel oil, also a highly reactive material, are somewhat more severe than required for production of a natural gas substitute; satisfactory results have been obtained at approximately twice the feed rate (one-half the residence time) than that employed in the test reported in Table 3.

Liquid product formation was on the order of 10 wt. % of the feedstock, and tended to increase with the C/H weight ratio of the feedstock at comparable operating conditions. The conversion efficiency of the process is indicated by net thermal recoveries of approximately 30 to 90% under the typical process conditions of Table 3; this parameter is a measure of the fraction of the heat of combustion in the feedstock which is recovered in the product gas.

EFFECTS OF PROCESS VARIABLES

The most effective control over hydrogasification product distribution can be exerted with the hydrogen to oil feed ratio. Table 4 shows that an increase in hydrogen feed ratio from 50 to 100% of stoichiometric reduced carbon formation from diesel oil from about 12% of the total weight of oil and hydrogen fed, to essentially zero; this was accompanied by a significant decrease in liquid products formation. Conversion to gas increased correspondingly. The gaseous product distribution (Figure 1) also changed considerably as 100% of stoichiometric feed ratio was approached, showing an abrupt increase in hydrogen breakthrough and a more gradual increase in ethane yield.

At 50% of stoichiometric feed ratio, there was little change in gaseous product distribution with increases in reactor pressure since the equimolar methane-ethane-hydrogen system was close to equilibrium at the long residence times employed. At 75 and 100% of stoichiometric feed ratio, the high ethane yields characteristic of aliphatic and alicyclic hydrocarbon hydrogenolysis systems were obtained,¹² and the hydrogen utilized for methane formation increased considerably with increases in pressure and corresponding increases in residence time.

The above results reflect the transition from control by pyrolysis reactions at the lowest feed ratio, to control by hydrogenolysis reactions at the highest feed ratio. The liquid products also reflect this transition. The proportion of benzene in the liquid products increased greatly with feed ratio, while the proportion of higher-boiling aromatics was greatly reduced.

Figure 2 correlates gaseous product yields from diesel oil with residence time, at approximately 100% of stoichiometric feed ratio. It can be seen that at residence times sufficient for completion of the primary gasification reactions as indicated by nearly constant net gasification (weight of product gas less weight of feed hydrogen, both per unit weight of feed oil), the gaseous product distribution was not affected by pressure over the 500-1500 p.s.i.g. range. This is characteristic of operating conditions where gas composition is primarily determined by the secondary, low molecular weight paraffin hydrogenolysis reactions: $C_n H_{2n+2} + H_2 \rightarrow CH_4 + C_{n-1} H_{2n}$, which appear to be pressure insensitive.

Further insight into the nature of the hydrogenolysis reactions can be gained from the data of Table 5 on the effect of temperature on conversion of the 0°-300°C. fraction of prehydrogenated Tapparito crude oil. Stoichiometric hydrogen feed ratio and 1500 p.s.i.g. were employed, and the diameter of the hydrogasifier was reduced to 2 inches to permit better temperature control over a 1100°-1400°F. range at four-fold variations in oil feed rate. Feedstock conversion to gas increased greatly with increases in temperature, and increased only slightly with increases in residence time. Low conversions to gas were accompanied by corresponding increases in liquid products and substantially lower

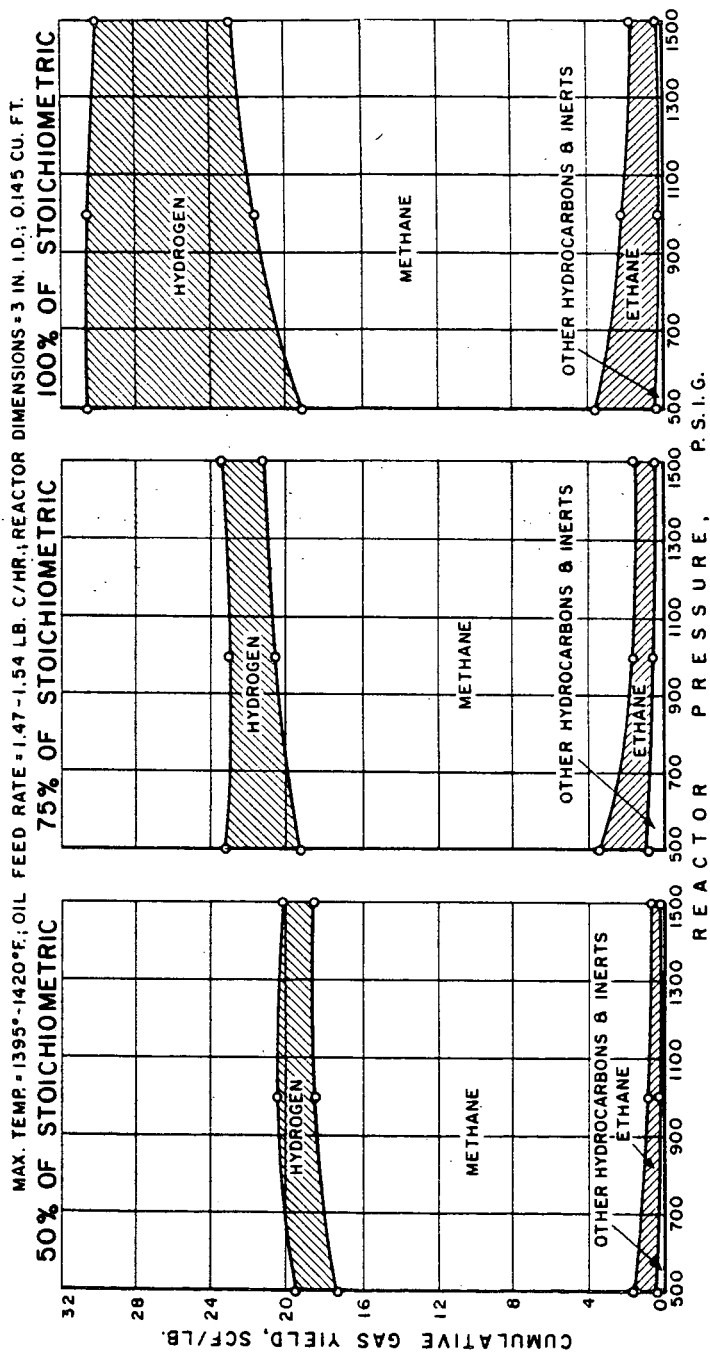


Figure 1.-EFFECTS OF HYDROGEN FEED RATIO AND PRESSURE ON GASEOUS PRODUCT YIELDS FROM DIESEL OIL

Table 4.-EFFECTS OF HYDROGEN FEED RATIO AND PRESSURE
ON HYDROGASIFICATION OF DIESEL OIL

Max. Temp.: 1395°-1420°F. Oil Feed Rate: 1.47-1.54 lb. C/hr.
Reactor Dimensions: 3 in. Inside Diameter, 0.145 cu.ft.

Pressure, p.s.i.g.	500			1000			1500		
Hydrogen feed ratio,	50.0	75.0	100.1	51.6	73.2	100.4	49.7	73.7	99.9
% of stoichiometric	153	131	99.5	298	254	196	443	375	501
Residence time, sec.									
Product distribution, %									
Gas	72.3	86.7	90.4	76.2	86.5	90.8	76.6	88.5	93.2
Liquid	15.9	12.1	9.6	11.5	12.2	9.2	11.2	9.7	6.8
Carbon	11.8	1.2	nil	12.3	1.3	nil	12.2	1.8	nil
Product liquid properties									
0°-160°C. fraction									
Wt. % of total	45.6	54.9	62.4	52.8	54.2	75.4	49.1	58.5	82.4
Benzene content, mole %	81.8	83.2	89.8	84.2	83.1	92.4	85.6	84.2	94.8
160°C.-plus fraction									
Wt. % of total	53.1	44.4	36.6	46.1	45.1	23.4	49.9	40.4	16.5
C/H wt. ratio	16.19	15.05	14.49	16.16	16.10	14.98	16.01	16.11	14.87

Table 5.-EFFECTS OF REACTOR TEMPERATURE AND OIL FEED RATE
ON HYDROGASIFICATION OF 0°-360°C. FRACTION
OF PREHYDROGENATED TAPARITO CRUDE

Feed Ratio: 98.0-102.5% of stoichiometric. Pressure: 1500 p.s.i.g.
Reactor Dimensions: 2 in. Inside Diameter, 0.0644 cu.ft.

Feed rate, lb. C/hr.	1.33			0.67			0.34		
Residence time, sec.	150-180			290-350			620-750		
Maximum temperature, °F.	1100	1300	1400	1100	1300	1400	1100	1300	1400
Product distribution, %									
Gas	75.2	86.2	89.9	75.1	87.1	91.9	79.1	89.2	92.3
Liquid	24.8	13.8	10.1	24.9	12.9	8.1	20.9	10.8	7.7
Carbon	nil	nil	nil	nil	nil	nil	nil	nil	nil
Gaseous product yields, SCF/lb.									
H ₂	21.8	14.3	9.7	20.9	14.3	9.1	17.3	10.6	6.2
CH ₄	4.1	10.9	18.7	5.2	12.7	20.3	5.9	15.0	21.6
C ₂ H ₆	2.7	5.1	1.8	3.3	4.5	1.1	3.7	3.3	0.5
C ₃ H ₈	1.5	0.1	--	1.3	--	--	1.1	--	--
Other	0.7	0.2	0.3	0.4	0.1	0.2	0.2	0.1	0.2
Product liquid properties									
0°-160°C. fraction									
Wt. % of total	41.7	70.1	72.3	49.3	66.4	71.1	59.6	68.6	81.0
Benzene content, mole %	31.7	92.7	94.9	52.2	91.0	94.4	71.5	95.4	94.9
160°C.-plus fraction									
Wt. % of total	56.8	29.2	26.3	49.1	32.3	27.8	37.8	30.4	17.6
C/H wt. ratio	10.66	13.90	15.53	11.96	13.94	15.74	14.58	15.83	15.60

FEED RATIO = 96.0-101.3% OF STOICHIOMETRIC
 MAXIMUM TEMPERATURE = 1395°-1445°F.

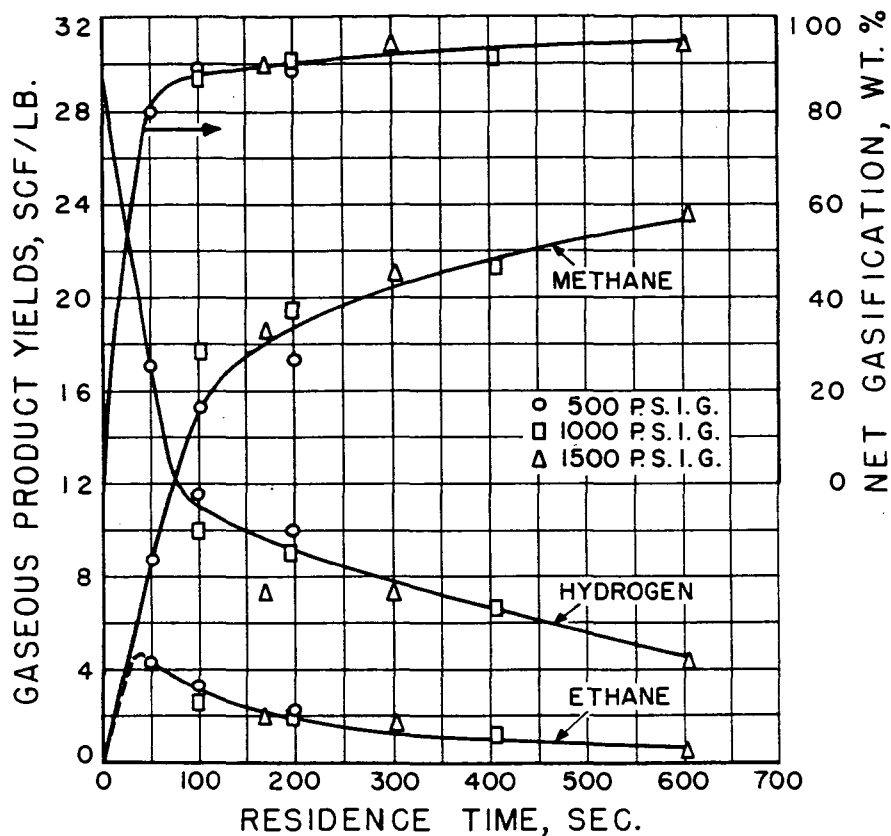


Figure 2.-EFFECTS OF RESIDENCE TIME
 ON GASEOUS PRODUCT YIELDS FROM DIESEL OIL

aromaticity of these liquid products. This was particularly evident in the highest feed rate run (shortest residence time) at 1100°F., where a substantial breakthrough of unreacted or partially converted feedstock was indicated by the low C/H weight ratio of the higher-boiling fraction of the liquid products, and the low benzene content of the lower-boiling fraction.

The gaseous product distributions in Table 5 clearly show the sequence of paraffin hydrogenolysis reactions leading to the formation of methane as the ultimate product. At 1100°F., ethane formation was still increasing toward its optimum value with increases in residence time, whereas at 1300° and 1400°F., ethane formation had passed its optimum. At 1100°F., propane formation had also passed its optimum within the range of residence times investigated. These trends are comparable with the results of previous batch reactor tests with low molecular weight paraffin hydrocarbons which indicated that, as temperature is increased, maxima in propane and ethane yields are obtained at approximately 1075° and 1200°F., respectively.¹²

INTEGRAL PROCESS CONCEPTS

Two hydrogen production schemes appear to be feasible for application in an integrated hydrogen production-prehydrogenation-hydrogasification process for conversion of crude and residual oils:

- 1) Catalytic steam reforming of a portion of the product gas, with reformer fuel requirements supplied by prehydrogenator recycle oil.
- 2) Partial oxidation (Texaco process⁴) of prehydrogenator recycle oil.

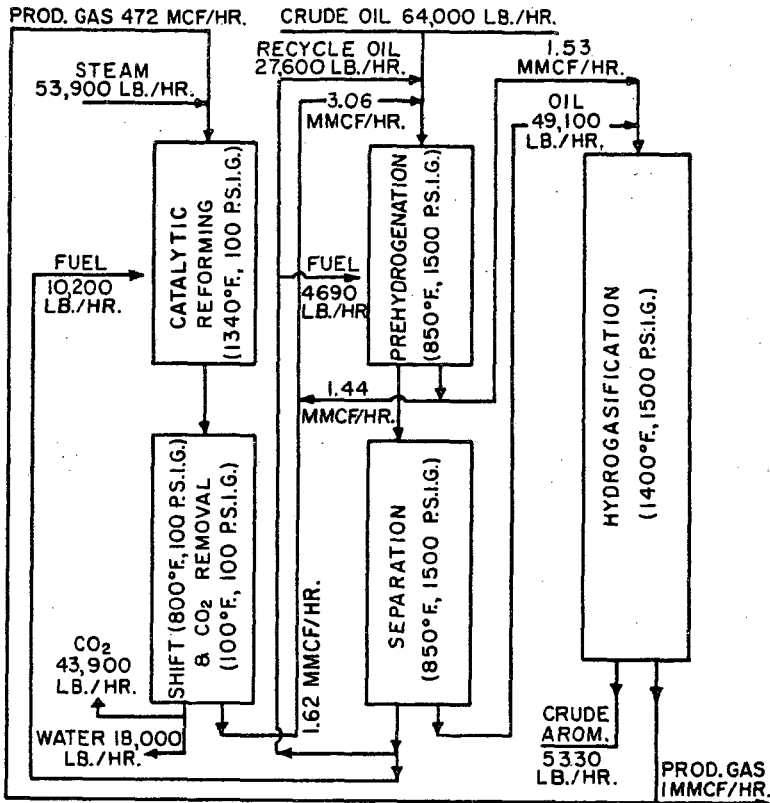
The flow diagrams of Figures 3 and 4, showing material requirements for all streams, are based on the production of 1 million SCF/hr. net pipeline gas from Taparito crude oil. A third integral process concept, not presented, would be autothermic catalytic reforming of product gas with steam and oxygen.

In Figure 3, the process gas feed supply for conventional catalytic steam reforming is provided by an increase in hydrogasification capacity of about 47% above that required for the net product gas yield. Fuel requirements for reforming are supplied with a portion of the prehydrogenator recycle oil.

When partial oxidation of prehydrogenator recycle oil is used for hydrogen production (Figure 4), somewhat less feed oil is required and byproduct aromatics production and prehydrogenation and hydrogasification duties are substantially reduced. Further, compression costs are considerably lower, since less make-up hydrogen and recycle hydrogen are used, and the pressure level of the hydrogen supply is higher (about 400 p.s.i.g. compared to about 100 p.s.i.g. for the reforming scheme). However, 276,000 SCF/hr. of oxygen must be supplied from an external source.

In the computations for Figures 3 and 4, actual data from Runs 80 and 89 (Tables 2 and 3) were employed for the prehydrogenation and hydrogasification steps. Published data for the Texaco partial oxidation step were used.⁴ Practical operating feed ratios of 3 moles of steam per mole of carbon to the reforming and shift steps in Figure 3, and 2 moles of steam per mole of CO to the shift step in Figure 4, were employed.^{5,10} For simplicity, complete conversion in the reforming and shift steps, and complete removal of CO₂ were assumed. Other assumptions made in these calculations are: saturated steam is available at 200 p.s.i.a. through waste heat recovery; fresh crude oil enters at 77°F.; reforming and preheat furnaces are 75% efficient.

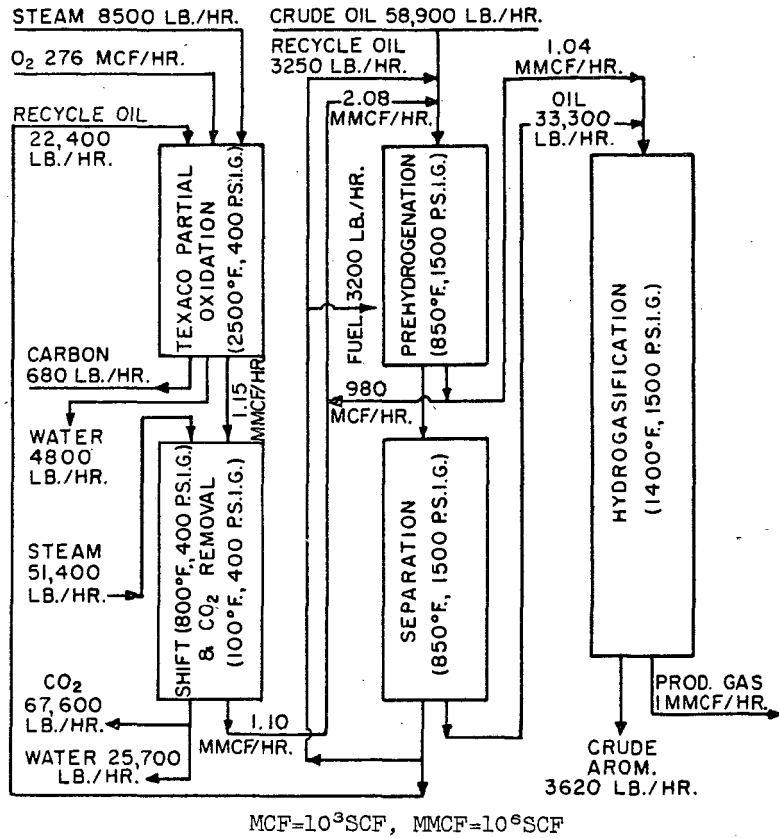
Assuming costs of \$2.50/barrel of feed crude oil and \$6.00/ton of oxygen, and a crude aromatics byproduct credit of 10 cents/gallon, net



MCF=10³SCF, MMCF=10⁶SCF

In, lb./hr.		Out, lb./hr.	
Oil	64,000	Product Gas	35,000
Steam	53,900	CO ₂	43,900
	117,900	Crude Aromatics	5,330
		Oil for Ref. Fuel	10,200
		Oil for Prehydrog. Preheat	4,700
		Water	18,000
		Loss	770
			117,900

Figure 3.-HYDROGEN PRODUCTION BY CATALYTIC STEAM REFORMING OF PRODUCT GAS



In, lb./hr.		Out, lb./hr.	
Oil	58,900	Product Gas	35,000
O ₂	22,900	CO ₂	67,600
Steam to Texaco	8,500	Crude Aromatics	3,620
Steam to Shift	<u>51,400</u>	Carbon from Texaco	680
	141,700	Water from Texaco	4,800
		Water from Shift	25,700
		Oil for Prehydrog. Preheat	3,200
		Loss	<u>1,100</u>
			141,700

Figure 4.-HYDROGEN PRODUCTION BY PARTIAL OXIDATION OF RECYCLE OIL

material costs of 55 and 60 cents/million B.t.u. net product gas were computed for the schemes of Figures 3 and 4, respectively. No estimate of other operating costs, or of investment costs, can be offered at this time.

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PRODUCTION OF PIPELINE GAS BY METHANATION OF
SYNTHESIS GAS OVER RANEY NICKEL CATALYSTS

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The technically most advanced method for the production of a high-heating-value (pipeline) gas from coal comprises gasification of the coal with steam and oxygen to a low-heating-value synthesis gas, followed by catalytic conversion of the hydrogen and carbon monoxide content of the purified synthesis gas to methane.^{1,23} The major effort has been expended on the gasification step because of its wide applicability. Fixed-bed and suspension gasification processes have been developed to a pilot plant scale,^{7,11,33,34} and some have been operated successfully on a commercial scale.^{15,17,21,36}

The methanation step has also been studied extensively, but much of the work has been concerned with catalyst development and, therefore, has involved small-scale experiments. In studies by the British Fuel Research and Gas Research Boards^{3,8-10} the development of fixed- and moving-bed reactors has been stressed. Initially, studies by the U.S. Bureau of Mines^{7,35} and the Institute of Gas Technology²³ were also conducted in relatively small fixed-bed reactors. In these investigations, supported nickel catalysts were employed nearly without exception.

The largest-scale fixed-bed methanation data for the production of high-heating-value fuel gas were reported by Dent and Hebden,⁸ who achieved near-equilibrium conversion of 3.6:1 H₂/CO ratio synthesis gas for 3500 hours in a 9.5-inch diameter by 10-inch deep catalyst bed at 20 atmospheres, 2000 std. cu. ft./cu.ft. catalyst-hr. fresh feed gas space velocity, and 6:1 recycle ratio. A coimpregnated nickel-alumina-china clay catalyst was employed.

The design of large-scale fixed-bed reactors for essentially complete conversion of hydrogen and carbon monoxide to methane at high throughputs presents difficult engineering problems. Large quantities of exothermic heat of reaction must be removed without causing excessive temperature gradients to occur in the catalyst bed. This requires either complex heat exchange equipment in the catalyst bed when a fluid coolant is used, or the use of high product gas recycle rates. In both instances, the investment and operating costs are high.

Fluid-bed reactors appeared to be better suited for the methanation process because of the high rates of heat transfer obtainable with relatively simple heat exchange equipment. The ease of addition and withdrawal of catalyst also seemed to be a significant advantage. However, restriction of the possible range of operating conditions by the fluidization characteristics of the solids-gas system employed, and catalyst attrition, were recognized as major problems. Further, scale-up of fluid-bed reactors for synthesis operations was known to be difficult¹⁶ and was not fully demonstrated on a commercial scale until recently.^{17,21}

In 1954, the U.S. Bureau of Mines achieved satisfactory fluid-bed operation in a 1-inch diameter reactor with a partially extracted Raney nickel catalyst;³¹ attempts to utilize fluid-bed iron catalysts

were not successful, and the performance of supported nickel catalysts was found to be difficult to reproduce.¹⁴ Russian investigators have also reported high conversion capacities of partially extracted Raney nickel catalysts in fluid-bed operation.^{4,5} A systematic study of this methanation technique was, therefore, initiated by the Institute of Gas Technology as part of its pipeline-gas-from-coal research program.

EXPERIMENTAL

In all of the work reported here, the catalysts were prepared by caustic leaching of 40-200 mesh Raney alloy with a nominal composition of 42 wt. % nickel and 58 wt. % aluminum.^{24,25} Synthesis gas was produced by catalytic steam reforming of natural gas in a tube furnace,²⁰ or by suspension gasification of coal with steam and oxygen in a slagging downflow pressure reactor.³⁴ Facilities were also available to increase the H_2/CO ratio of synthesis gas produced from coal from the usual 1:1-1.5:1 range to 3:1 by catalytic conversion of CO with steam to form H_2 and CO_2 . In some instances, CO_2 from bottle storage was added to the 3:1 H_2/CO ratio reformed natural gas to simulate the composition of synthesis gas from coal after CO shift and before CO_2 removal.

Except for a limited number of tests of sulfur tolerance, synthesis gas was purified, by passage through fixed beds of iron oxide and activated carbon, to a sulfur content of less than 0.01 grain per 100 SCF (standard cubic foot at 60°F., 30 inches of mercury and saturated with water vapor), and generally to about 0.001 grain per 100 SCF. Details of the analytical procedures for determination and identification of sulfur compounds in synthesis gas have been presented elsewhere.^{22,28,32}

Three major methods of operation were employed in the study of fluid-bed methanation of synthesis gas over Raney nickel catalysts:

1. Catalyst evaluation tests and process variable studies in a battery of approximately 1-inch inside diameter Dowtherm-jacketed reactors (Figure 1). The effect of catalyst preparation on initial activity and total methane production capacity was determined with purified synthesis gases of approximately 3:1 H_2/CO ratio, and either negligible or 30 mole % average CO_2 content. Nominal test conditions were: 10,000 SCF/cu.ft. catalyst-hr. space velocity, 75, 150 and 300 p.s.i.g. reactor pressure, and 100 cc. initial alloy volume. (Space velocities are based on the initial dry alloy volume). A systematic study was also made of the variables of synthesis gas H_2/CO ratio, synthesis gas CO_2 and organic sulfur content, space velocity and operating pressure. Catalyst bed temperature was controlled by adjustment of pressure in the Dowtherm-jacket and reflux condenser, with the Dowtherm maintained at the boiling point by an electric heater surrounding the jacket. Temperatures, although difficult to maintain constant throughout the bed because of the high exothermicity of the reaction, were normally within 700°-800°F.

2. Capacity tests of a 6-inch inside diameter pilot plant reactor (Figure 2). Dowtherm "A" circulating through an external jacket and through six internal bayonets was used to heat the catalyst to reaction temperature at the start of operation, and then, as increasing quantities of exothermic heat of reaction were released, to remove heat from the catalyst bed. This was accomplished by controlling the Dowtherm temperature between the limits of 750°F. (corresponding to a vapor pressure of 144 p.s.i.g.) and 496°F. (the atmospheric boiling point) with a gas-fired heater upstream from the reactor, and a flash chamber and reflux condenser downstream from the reactor. The flash temperature was controlled with a nitrogen back-pressure system. The high circulation rate (30 gal./min.) allowed most of the Dowtherm to remain in liquid form. Purified synthesis gas produced by catalytic steam

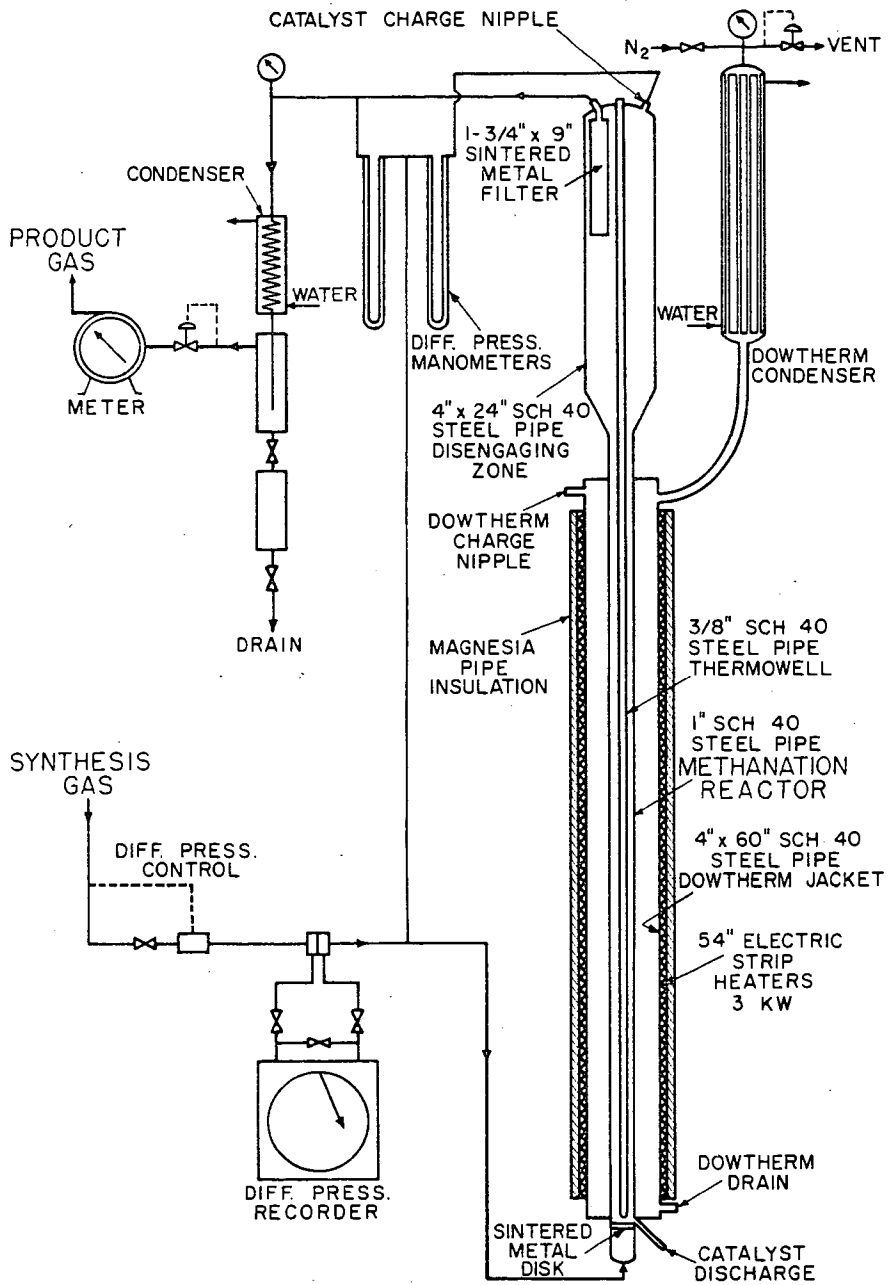


Fig. 1.-LABORATORY FLUID-BED METHANATION UNIT

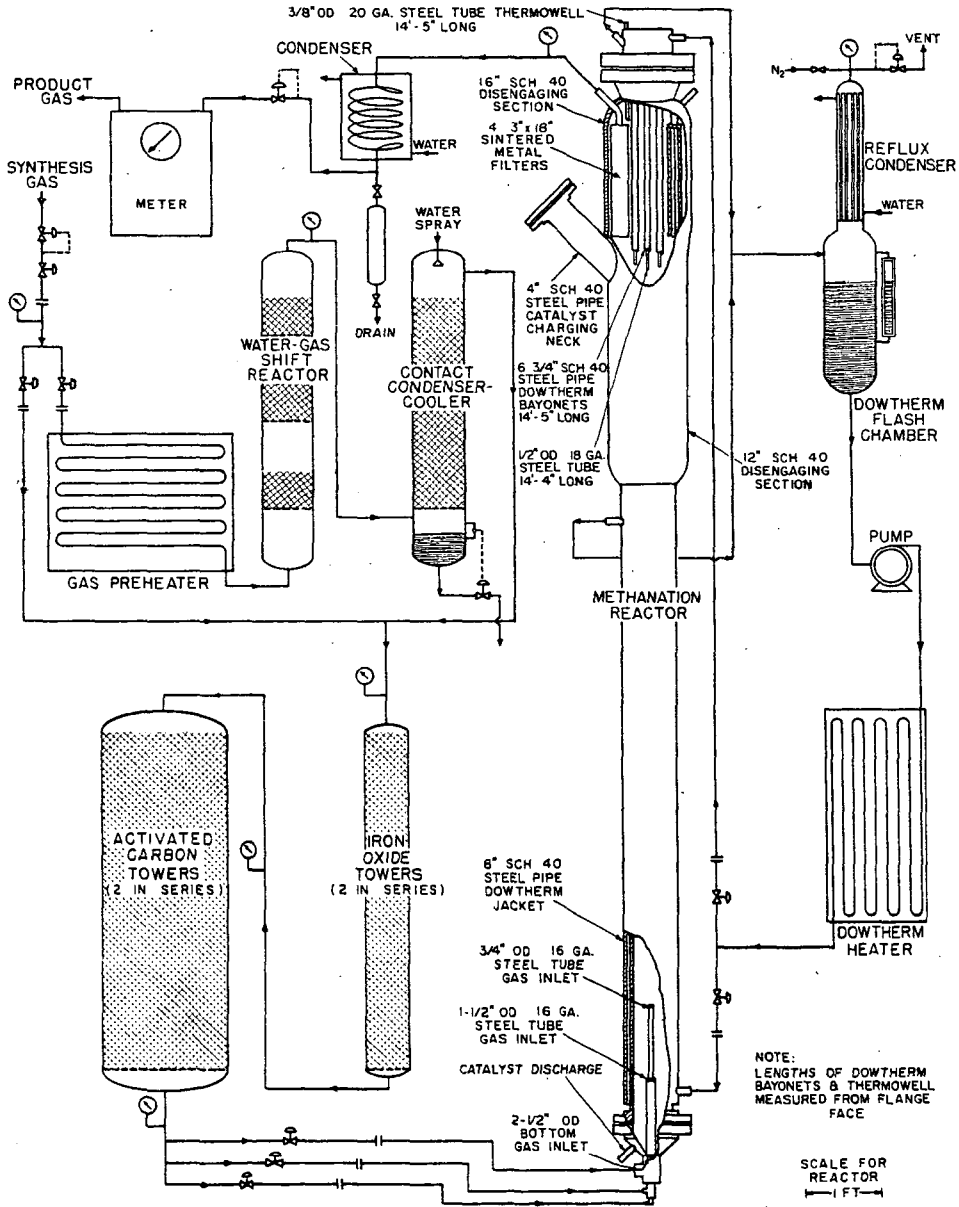


Fig. 2.-FLUID-BED METHANATION PILOT UNIT

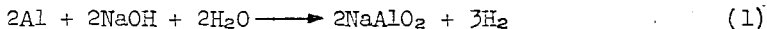
reforming of natural gas was used as feed at pressures up to 190 p.s.i.g. After a series of short tests, comprising 177 hours of steady-state operation with a batch of catalyst prepared from 0.343 cu.ft. of alloy, the reactor was slightly modified to the design depicted in Figure 2 to permit attainment of a synthesis gas capacity of 3000 SCF/hr. with a 0.5 cu. ft. catalyst charge; initially, the cooling bayonets were constructed of 1/2-inch Schedule 40 pipe, the disengaging section was smaller, and the porous stainless steel gas filters were also smaller and located in a side offtake.

3. Exploratory pilot plant tests of simulated integrated pipe-line-gas-from-coal operation involving the process steps of a) suspension gasification of coal with steam and oxygen to produce synthesis gas at a nominal rate of 20,000 SCF/hr., b) preliminary purification with iron oxide for bulk removal of hydrogen sulfide, c) temporary pressure storage and withdrawal at 3000 SCF/hr., d) adjustment of synthesis gas composition by partial carbon monoxide shift of a portion of the synthesis gas, e) final purification with iron oxide and activated charcoal to less than 0.01 grain of sulfur per 100 SCF, and f) methanation over fluidized Raney nickel catalyst in the reactor depicted in Figure 2.

CATALYST PREPARATION AND HANDLING

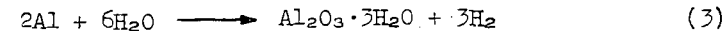
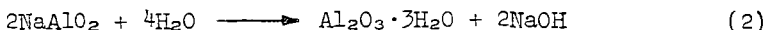
The 42 wt. % nickel-58 wt. % aluminum alloy was supplied by the Raney Catalyst Company. The structure of the crushed alloy is shown in Figure 3. The highly fractured condition of the catalyst particle is typical of the material used in the test program. The dark homogeneous regions are Ni_2Al_3 (gamma) phase, the light homogeneous regions are $NiAl_3$ (beta) phase, and the elongated mottled regions are a fine-grained eutectic mixture consisting of alpha phase (less than 0.05 wt. % nickel) and beta phase. Metallographic studies of caustic-etched particles showed that the gamma phase is more resistant to attack than are the other two phases, although x-ray analyses of caustic-treated alloy indicated the presence of all of the three original phases even when the aluminum content had been reduced to 5 wt. % or less. The major product of caustic leaching recovered in the catalyst was identified by x-ray as beta-alumina-trihydrate, and the presence of small crystallites of metallic nickel was also indicated when the aluminum conversion by caustic leaching was substantial.

Originally, the activation procedure reported by the U. S. Bureau of Mines was employed.³¹ This procedure was based on the assumption that an active catalyst could be prepared by extraction, with dilute caustic, of only 3-5 % of the aluminum content, and that the amount of aluminum removed was determined by a stoichiometric relationship such as:²⁵



It was further assumed that this procedure could be repeated a number of times to restore the activity of the catalyst.

After development of the necessary analytical techniques, it was shown in this study that at least 20% of the aluminum had to be converted before significant activity for the methanation reaction was obtained, and that considerably higher conversions were required to produce a long-lived catalyst. Further, the presence of large amounts of $Al_2O_3 \cdot 3H_2O$ in the extracted alloy confirmed that in addition to Reaction (1), sodium aluminate or direct aluminum hydrolysis reactions occur:²⁵



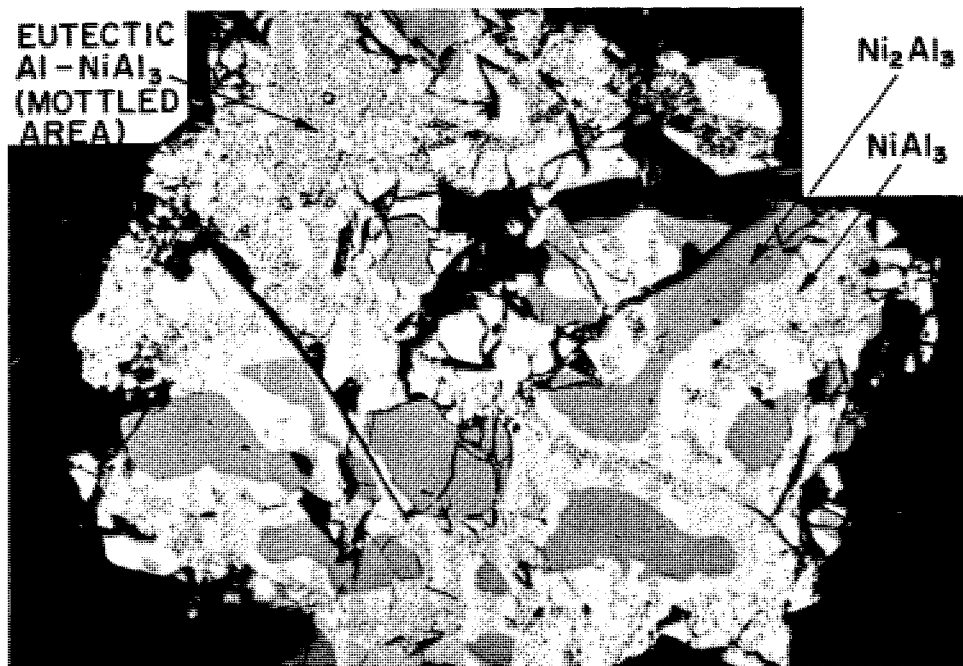


Fig. 3.-MICROSTRUCTURE OF 42 WT.% NICKEL - 58 WT.% ALUMINUM ALLOY (X 500)

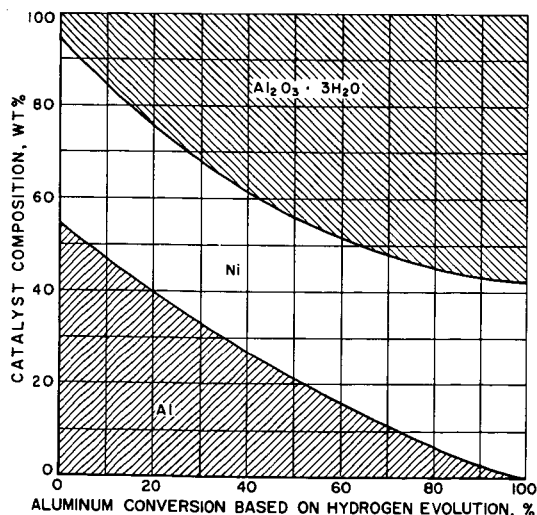


Fig. 4.-COMPOSITION OF RANEY NICKEL CATALYSTS PREPARED BY CAUSTIC LEACHING AT CONTROLLED RATE AND AMOUNT OF HYDROGEN EVOLUTION

Efforts to reduce aluminum oxide formation under conditions allowing only partial aluminum conversion were not successful. (In commercial Raney nickel catalyst preparation,²⁵ the alloy is added to an excess of concentrated caustic which apparently favors aluminum removal as aluminate.)

Since 3 moles of hydrogen are evolved per 2 moles of aluminum converted to either aluminate or alumina, it was possible to follow the progress of catalyst activation by measurement of hydrogen evolution. In the standard procedure for preparing laboratory batches of catalyst, 100 cc. (162 g.) of 42 wt. % nickel-58 wt. % aluminum alloy and 280 cc. of water were placed in a 2-liter three-neck flask. One neck of the flask held a mercury thermometer, the center neck held a reflux condenser, and the third neck held a buret for caustic or quench water addition. A wet-test meter was connected to the reflux condenser to measure the evolved hydrogen. A magnetic stirrer was used to slightly agitate the alloy. Fifteen cc. of a 26 wt. % sodium hydroxide solution was added, causing hydrogen evolution to begin, accompanied by a large heat release. When the temperature reached the boiling point after about 8 to 12 minutes, enough water was added to prevent flash vaporization, but not enough to reduce the temperature below the boiling point. The reaction was permitted to proceed at the boiling point until either an apparent 30, 65 or 85% of aluminum conversion had occurred. For example, the 2.88 SCF of hydrogen corresponding to 65% of apparent aluminum conversion of 162 g. of alloy was evolved in 34 to 42 minutes. At the desired point, the reaction was quenched by the addition of large amounts of cold water and the caustic liquid decanted from the wet catalyst. The catalyst was washed neutral to litmus and stored in methanol.

Figure 4 shows the relationship between chemical analysis of the catalysts prepared in accordance with the standard procedure, and the percent of aluminum conversion indicated by hydrogen evolution. It was necessary to further develop conventional procedures^{9,18} to make these analyses. The most reliable technique consisted of drying the sample by heating in a stream of dry hydrogen, and passing dry hydrogen chloride over it to volatilize the aluminum metal as aluminum chloride. The aluminum chloride was recovered, precipitated with ammonia, and ignited to the oxide. The residue from the hydrogen chloride treatment was boiled with nitric acid, and filtered. The residue from the filtration was ignited to obtain the quantity of alumina not dissolved by this treatment. The filtrate was diluted to volume; on one aliquot, alumina was determined by double precipitation with benzoate and ignition to the oxide; on another aliquot, nickel was determined by dimethylglyoxime.

Batches of pilot plant catalysts were prepared only by the original activation method, which consisted of leaching a suspension of the alloy in water at a maximum temperature of 120°-130°F. by slow addition of sufficient dilute sodium hydroxide solution to convert 5% of the aluminum content in accordance with Reaction (1). After 4 to 6 hours, vigorous hydrogen evolution stopped, and the catalyst was washed neutral to litmus and stored in water. No reliable analyses of pilot plant catalysts are available, since the analytical technique had not been fully developed at that time.

The particle size distribution of the alloy used in the preparation of laboratory batches was standardized by combining individual screen fractions in the fixed proportions shown below; the screen analysis of the 0.343 cu. ft. of alloy for the original pilot plant batch is also given:

U.S.S. Sieve	Alloy Size Distribution, Wt. %	
	Standard Laboratory Charge	Pilot Plant Charge
+40	0	1.2
-40 + 60	15	15.8
-60 + 80	15	10.1
-80 + 100	10	9.7
-100 + 140	35	34.7
-140 + 200	25	28.3
-200	0	0.2

In the pilot plant study, the prepared catalyst was charged as a water slurry and, in the majority of the laboratory tests, as a methanol slurry. Charging was done under a nitrogen blanket. Transfer as a slurry was used to avoid the possibility of catalyst oxidation, which could result in catalyst deactivation. After the slurry had been charged into the reactor, it was dried in a stream of nitrogen before introduction of synthesis gas. The catalyst temperature was raised to a level not exceeding 650°F., which was sufficient to initiate reaction of the synthesis gas, causing further temperature rise which had to be controlled by adjustment of the Dowtherm temperature level. Since the reactors were shut down repeatedly without change of the catalyst charge, it was necessary to store the catalyst in the reactor under nitrogen. In case of extended tests which were interrupted only temporarily, such as by scheduled weekend shutdowns, the catalyst temperature was maintained at 400°-500°F.

In catalyst life tests, the above charging and startup procedures gave exceedingly poor reproducibility of results. Rapid loss of catalyst through the porous stainless steel filters occurred in many attempts to make an extended run; the particles escaping from the reactor were very small and only a minor portion could be recovered. A common occurrence which preceded an abrupt reduction in conversion capacity was lifting of the bed into the disengaging zone and deposit on the filters, requiring blow-back to reduce pressure; this frequently took place after a weekend shutdown. No specific cause for this type of failure could be established, but it was found that by making the following revisions in these procedures it was possible to greatly improve the consistency of the catalyst performance data:

1. Store in methanol for not longer than 24 hours.
2. Predry in nitrogen at 250°F. for 2 hours to obtain free-flowing material.
3. Charge to unit under nitrogen blanket.
4. Start up slowly with hydrogen as fluidizing medium at approximately 1 ft./sec. superficial velocity, and gradually replace hydrogen with synthesis gas after attainment of the desired temperature and pressure.
5. During interruption of an extended test, shut down in nitrogen at 450°F. and atmospheric pressure and start up with hydrogen as above.

PROCESS VARIABLES

A number of thermodynamic analyses of the methanation reaction system have been made^{3,9,14,23} in an effort to evaluate the influence of the major operating variables: pressure, temperature and H₂/CO ratio,

on the equilibrium conversion of the feed gas to methane, water vapor, carbon dioxide and carbon. In these analyses the chemical reactions:



were employed as the basis of the equilibrium product distribution calculations. Under conditions of chemical equilibrium in the absence of carbon formation, any two of the first three reactions will define the system. When equilibrium carbon formation is to be included, one of the three carbon-forming Reactions (7), (8) and (9) must also be considered. The results of the various thermodynamic studies show that in the absence of carbon formation, nearly stoichiometric conversion of 1:1 to 3:1 H_2/CO ratio synthesis gases to methane can be attained at 650°F. and 25 atmospheres (353 p.s.i.g.); equilibrium methane yields decrease with increases in temperature and decreases in pressure, but remain reasonably high below 900°F. at pressures from 1 to 25 atmospheres.

The calculation of equilibrium carbon yields is complicated by lack of information on the nature of the carbon deposited on methanation catalysts. Standard thermodynamic data are normally based on carbon in the form of beta-graphite²⁷, whereas under actual experimental conditions the deposited carbon may be in different forms, and, therefore, have different thermodynamic properties. For example, removal of excessive carbon from the system may involve carbide formation with the metallic catalyst component.

Carbon deposition boundary data based on equilibrium constants obtained from actual methanation reaction systems catalyzed by precipitated nickel⁹ show substantially lower limiting feed gas H_2/CO ratios than data based on beta-graphite.¹⁴ For example, at 900°F., the minimum H_2/CO ratios calculated from the experimental equilibrium data are 1.75:1 at one atmosphere, and 1.5:1 at 25 atmospheres. In comparison, when beta-graphite is used as the form of carbon, the minimum H_2/CO ratios at 900°F. are 3.25:1 at one atmosphere, and 2.6:1 at 25 atmospheres. For the calculations based on experimental results, the limiting H_2/CO ratio drops to 1:1 at 600°F., whereas for the beta-graphite data, freedom from carbon formation is not indicated anywhere in the low-temperature range below H_2/CO ratios of 2.6:1. Addition of steam or CO_2 to the feed gas lowers the limiting H_2/CO ratios.

The presence of CO_2 in the feed also has the desirable tendency to suppress hydrogen breakthrough. For example, if only the stoichiometric relationships are considered, a 3:1 H_2/CO ratio feed gas could give methane yields ranging from 0.125 moles to 0.25 moles/mole $\text{H}_2 + \text{CO}$, while complete CO conversion is maintained. Thus, unless CO conversion via the CO_2 -forming Reactions (5) or (6) is limited by equilibrium hindrance, the actual methane yield may be substantially below the theoretically attainable level.

To establish the range of suitable fluid-bed operating conditions with Raney nickel catalysts, a series of exploratory tests was made in the laboratory reactors. Synthesis gases of about 1.5:1 and 3:1 H_2/CO ratio and various CO_2 contents were methanated over catalyst charges prepared by leaching of 100 cc. of alloy with dilute caustic for more than 4 hours. Pressure levels of 27, 75 and 150 p.s.i.g. were investigated, which permitted up to fourfold variations in space velocity at constant superficial feed gas velocity. With purified synthesis gas produced by steam-oxygen gasification of coal (42-47 mole % H_2 , 31-32 mole % CO, 15-19 mole % CO_2 , 1-2 mole % CH_4 , 4-5 mole % N_2) complete CO and nearly complete

H₂ conversions were obtained at superficial feed gas velocities up to approximately 0.7 ft./sec. This corresponds to a space velocity of 8000 SCF/cu. ft. catalyst-hr. at 150 p.s.i.g. At superficial velocities below 0.3 ft./sec., carbon recoveries in the product gas tended to be low, possibly as a result of carbon deposition on overheated, incompletely fluidized catalyst.

In a series of parallel tests with 2.8-3.4:1 H₂/CO ratio synthesis gases containing only small amounts of CO₂, CH₄ and N₂, no significant CO breakthrough was observed at space velocities as high as 9000 SCF/cu. ft. catalyst-hr. at 27 p.s.i.g., and 15,000 SCF/cu. ft. catalyst-hr. at 75 and 150 p.s.i.g. Satisfactory operation in all other respects was also obtained over a superficial feed gas velocity range of 0.1-3.3 ft./sec., except for one instance of apparent low carbon recovery in the product gas at 0.1 ft./sec. and 150 p.s.i.g.

In an additional series of tests, the effect of 20-30 mole % CO₂ dilution of 3.2-3.8:1 H₂/CO synthesis gas was investigated at pressures of 75, 150 and 300 p.s.i.g. At gas feed rates corresponding to space velocities of 7000-23,000 SCF/cu. ft. catalyst-hr. and superficial velocities of 0.2-2.4 ft./sec., no significant CO breakthrough was observed, and carbon recoveries in the product gas were approximately 100%.

The 1.049-inch inside diameter reactors used in the last series and in subsequent tests had approximately 60% more annular space than the reactors used initially, since the diameter of the thermowell had been decreased from 0.840 inches to 0.675 inches. As a result, catalyst bed depths and superficial gas velocities at equivalent operating conditions were about 60% of the values with the original reactor design. This was probably responsible for an increase in the maximum temperature level of the catalyst bed from 650°-750°F. to 690°-790°F. under conditions giving essentially complete CO conversion.

A summary of the average yield data for these three series of tests is presented in Table 1. The data show the expected trend of increase in methane content, and decrease in hydrogen content, of the product gas as pressure is increased. At 75 p.s.i.g., there was little suppression of hydrogen breakthrough due to the effects of feed gas CO₂ content. However, at 150 p.s.i.g., substantial reduction in hydrogen breakthrough was observed at the lower space velocities. At 300 p.s.i.g., the combined effect of high pressure and presence of CO₂ in the feed gas resulted in nearly complete suppression of hydrogen breakthrough except at the very high space velocities. The tendency toward increases in hydrogen breakthrough with increases in space velocity for the high H₂/CO ratio synthesis gases was not clearly defined at all pressure levels, possibly due to variations in feed gas composition. In the tests with the high CO₂-content 3:1 H₂/CO ratio gases there was a slight reduction in the quantity of CO₂ leaving the reactor compared to the quantity entering.

Although only some of the product gases had CO concentrations readily detectable by the analytical procedures employed (mass spectrometer supplemented by infrared analysis), it appears that the carbon monoxide shift reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ closely approached equilibrium in all tests, since CO concentrations of less than 1 mole %, and normally as low as 0.1-0.5 mole %, would give experimental equilibrium constants consistent with the theoretical values.

CATALYST PERFORMANCE

The important catalyst performance variables are activity and total conversion capacity. In this study, activity is defined in terms of the percentage of the synthesis gas H₂ + CO content that is converted to methane

Table 1.-EFFECT OF OPERATING CONDITIONS ON FLUID-BED
METHANATION YIELDS WITH RANEY NICKEL CATALYST

CO₂-Containing 1.5:1 H₂/CO Ratio Feed Gas

Pressure, p.s.i.g.	27	75	150
Space velocity, SCF/cu. ft.	1200-	2300-	3000-
cat.-hr. ^a	2200	4400	8000
Moles product gas/mole feed	0.56	0.56	0.55
Moles water formed/mole feed	0.07	0.07	0.07
Gas composition, mole %	Feed	Feed	
CO ₂	16	16	53
CO	31	32	--
H ₂	47	46	2
CH ₄	1	1	36
N ₂ ^b	5	5	10

Essentially CO₂-Free 3:1 H₂/CO Ratio Feed Gas

Pressure, p.s.i.g.	27	75	150
Space velocity, SCF/cu. ft.	1000-	1000-	1000-
cat.-hr	9000	15,000	15,000
Moles product gas/mole feed	0.30	0.30	0.27
Moles water formed/mole feed	0.23	0.23	0.24
Gas composition, mole %	Feed		
CO ₂	1	6	5
CO	24	--	--
H ₂	74	11-14	11
CH ₄	0	78-75	78
N ₂ ^b	1	5	5

CO₂-Containing 3:1 H₂/CO Ratio Feed Gas

Pressure, p.s.i.g.	75	150	300
Space velocity, SCF/cu. ft.	8000-	7000-	7000-
cat.-hr	23,000	21,000	17,000
Moles product gas/mole feed	0.45	0.45	0.43
Moles water formed/mole feed	0.20	0.20	0.21
Gas composition, mole %	Feed		Feed
CO ₂	27	56	25
CO	16	--	17
H ₂	56	5	57
CH ₄	0	36	0
N ₂ ^b	1	3	1

^aSpace velocities outside this range gave either less than 90% carbon recovery in the product gas or substantial CO breakthrough.

^bReported N₂ content of product gases may include small percentage of CO.

or methane equivalent: % H₂-CO Conversion =

$$100 \frac{4 \left[\frac{(\text{Moles Dry Prod. Gas})}{(\text{Moles Dry Feed Gas})} \left(\frac{\text{Mole \% CH}_4\text{-Equiv. in Dry Prod. Gas}}{\text{Mole \% H}_2 + \text{CO in Dry Feed Gas}} \right) - \left(\frac{\text{Mole \% CH}_4\text{-Equiv. in Dry Feed Gas}}{\text{Mole \% H}_2 + \text{CO in Dry Feed Gas}} \right) \right]}{1}$$

where the methane-equivalent is the sum of: mole percentage multiplied by carbon number for each gaseous hydrocarbon. At complete conversion to methane of any synthesis gas in the 1:1-5:1 H₂/CO ratio range by the necessary combination of Reactions (4) and (5), or (4) and (6), a value of 100% would be obtained. If ethane is also produced, the H₂-CO conversion based on the above definition could slightly exceed 100%; however, the maximum value at complete conversion of 0.75:1-2.5:1 H₂/CO ratio synthesis gases to ethane would be only 114%. The total conversion capacity of the catalyst is defined as the weight of net methane equivalent per unit weight of original alloy nickel content, or the volume of net methane equivalent per unit weight of original alloy, produced by the catalyst during the period in which it maintains 70% H₂-CO conversion or more.

Sulfur tolerance limits of standard fluid-bed Raney nickel catalysts prepared by 65 and 85% aluminum conversion were determined to establish synthesis gas purification requirements. In these tests, CO₂-containing, 3:1 H₂/CO ratio synthesis gases having organic sulfur contents (mainly in the form of COS) of 0.5 to 4 grains per 100 SCF were methanated at space velocities of 5000 to 15,000 SCF/cu.ft. catalyst-hr. and 75 p.s.i.g. Each test was made with a fresh batch of catalyst, and continued until most of the catalyst activity had been lost. It was observed that the catalyst activity dropped rapidly to less than 70 to 80% H₂-CO conversion when the total sulfur exposure attained a level of approximately 0.5 lb./100 lb. of nickel. This agrees quite well with similar sulfur poisoning test results obtained in studies with supported nickel catalysts.³⁵ It was determined by measurement of H₂S and organic sulfur liberated from a poisoned catalyst by acid treatment that essentially all of the organic sulfur introduced in the course of a test was removed by the catalyst. From a linear extrapolation of these results, adequate catalyst activity could be expected for about 1500 hours when a gas containing 0.01 grain of sulfur per 100 SCF is fed at a rate of 10,000 SCF/cu.ft. catalyst-hr.

Typical results of a catalyst life test with purified synthesis gas are given in Table 2. In this test, H₂-CO conversion dropped to approximately 80% in 1010 hours of operation at 75 p.s.i.g.; at that time, the pressure level was increased to 150 p.s.i.g., which resulted in an increase in H₂-CO conversion to a level of about 90%. However, after 1300 hours of operation, the H₂-CO conversion dropped to 70% and the run was terminated. Only 45% of the original catalyst volume (measured under methanol) was recovered, so the decrease of conversion capacity cannot be ascribed solely to activity loss.

The CO₂-free heating values shown in Table 2 are lower than would be desirable for use of the process as a source of a natural gas supplement. This is typical of operation at relatively low pressure and high space velocity with a high H₂/CO ratio synthesis gas. However, gas of approximately 900 B.t.u./SCF CO₂-free heating value was produced for about 500 hours in a similar run in which the pressure was maintained at 150 p.s.i.g. through the entire operating period. By adjustment of the H₂/CO ratio to minimize hydrogen breakthrough, and reduction of the nitrogen content of the synthesis gas, it is also possible to produce 900 B.t.u./SCF CO₂-free gas at 75 p.s.i.g. and 10,000 SCF/cu.ft. catalyst-hr. space velocity for limited periods.

Table 2.-TYPICAL PERFORMANCE DATA FOR STANDARD FLUID-BED RANEY NICKEL CATALYST^a

Duration of test, hr.	300	500	720	970	1070	1300
Feed gas						
H ₂ /CO ratio	2.98	3.12	3.22	3.28	3.05	3.65
Sulfur, grains/100 SCF	0.0010	0.0004	0.0005	0.0007	0.0005	0.0008
Pressure, p.s.i.g.	75	75	75	75	150	150
Temperature, °F.						
Bottom of reactor	790	725	735	710	750	685
9 inches from bottom	795	770	780	775	800	755
18 inches from bottom	785	780	780	795	795	800
27 inches from bottom	785	780	780	795	790	790
Feed gas						
Space velocity, SCF/cu.ft. cat.-hr	11,578	11,556	12,248	11,981	10,210	10,584
Superficial inlet velocity, ft./sec. ^b	1.27	1.20	1.29	1.20	0.59	0.58
Product gas ^b						
SCF/SCF feed	0.495	0.506	0.499	0.522	0.488	0.573
Carbon recovery, %	100	98	100	98	100	100
Hydrogen recovery, %	66	68	71	68	69	69
Oxygen recovery, %	80	79	76	79	77	82
Composition, mole %						
CO ₂	Feed 28.1	Feed 26.9	Feed 22.5	Feed 23.3	Feed 25.7	Feed 44.7
CO	17.7	16.3	17.3	16.9	17.6	25.2
H ₂	52.7	50.9	55.7	55.5	53.7	15.6
CH ₄	0.3	3.6	7.1	11.8	2.7	5.4
C ₂ H ₆	--	0.1	2.3	28.9	5.9	24.4
N ₂	1.2	2.2	0.3	0.9	0.6	22.2
Total	100.0	100.0	100.0	100.0	100.0	100.0
CO ₂ -free specific gravity, air = 1.000	0.528	0.505	0.484	0.442	0.514	0.407
CO ₂ -free heating value, B.t.u./SCF	856	840	784	701	863	584
Water formation, moles/mole feed gas						
By hydrogen balance	0.1821	0.1852	0.1796	0.1875	0.1736	0.1820
By oxygen balance	0.1486	0.1470	0.1487	0.1441	0.1651	0.1230
H ₂ -CO conversion, %	92	86	87	78	94	68

^a Run No. 498, Catalyst No. 59B prepared by 65% aluminum conversion of 100 cc. (162g.) of 40-200 mesh 42 wt. % nickel-58 wt. % aluminum alloy.

^b Excluding water formed by methanation reactions.

Table 3 summarizes the test results for five extended runs in which more than 1000 lb. net CH_4 -equivalent/lb. Ni was produced. Included are results of an early test with a catalyst which was activated by three successive caustic extractions (No. 25C). It can be seen that the conversion capacities obtained after the first two extractions were very small. Extended operation was possible only after most of the aluminum had been extracted. This run was discontinued voluntarily before the H_2 -CO conversion had decreased to the minimum acceptable level. In a test with another early catalyst preparation (No. 33A) it was possible to obtain a total conversion capacity of 2770 lb. net CH_4 -equivalent/lb. Ni by successive pressure increases from 75 to about 300 p.s.i.g. The attrition rate in this test was the lowest of any completed so far; unfortunately, the analytical data for Catalyst 33A are not reliable, since they were obtained at a time when the procedures were still under development. For example, the significant difference in the composition of fresh and recovered catalyst was not observed in the three most recent tests (Catalysts 66B, 59B and 59A2). It has also not been possible to reproduce the composition of fresh Catalyst 33A, which shows an unusually high nickel and low alumina content.

On the basis of the data of Table 3, at the currently quoted cost of 90 cents per lb. for pulverized 42 wt. % nickel-58 wt. % aluminum Raney alloy in 25,000 lb. lots,²⁸ alloy costs per 1000 SCF of methane-equivalent would be in the range of 3 to 6 cents, assuming no nickel credit for the spent catalyst. If these results could be duplicated on a commercial scale, catalyst costs should not be a major factor in determining the final cost of producing pipeline gas from coal via the methanation process.¹⁸

PILOT PLANT TESTS

The fluid-bed pilot unit was operated intermittently over a period of ten months with the original 0.343 cu. ft. charge of caustic-extracted 42 wt. % nickel-58 wt. % aluminum Raney catalyst. Nine runs with steady-state periods ranging from 7 to 47-1/2 hours were made with a cumulative steady-state operating period of 177 hours. During this time, approximately 47,000 SCF of net methane-equivalent, corresponding to 125 lb./lb. Ni, were produced. Typical operating data from this series of runs are given in Table 4.

The alloy used in the preparation of the pilot plant catalyst had a bulk density of approximately 110 lb./cu. ft. Assuming no volume change during extraction, the static bed height in the reactor would have been approximately 2 feet. It appears from the temperature patterns observed in the reactor at the higher feed rates that the actual bed height during operation was approximately 3 feet.

The feed gas was introduced through the two lower inlets, with 2/3 or more fed at the bottom of the reactor, and the remainder at the 18-inch level. Pressure levels in the reactor were generally increased with increases in feed rate, so that the superficial bottom feed gas velocity was maintained in the 0.2-0.6 ft./sec. range (calculated on the basis of inlet temperature, reactor pressure and cross-sectional area of the empty reactor). To maintain product gas quality as throughput rate and pressure were increased, it was necessary to increase the catalyst bed temperature from approximately 700°F. at space velocities of less than 1000 SCF/cu. ft. catalyst-hr. to 900°F. at space velocities of 5000 to 6000 SCF/cu. ft. catalyst-hr.

Table 3.-SUMMARY OF CATALYST LIFE TEST RESULTS

Catalyst No.	407	409	25c	411	66B	59B	59A2	33A
Run No.	160	174		180	516	498	511	444
Catalyst preparation								
Maximum temperature, °F	25	32		48	205	204	206	208
Activation duration, min	24	24		23	32	74 ^a	74 ^a	More than
Aluminum conversion, %	No	No		No	65	65	65	4 hr
Predrying in N ₂					2 hr. at	No	2 hr. at	No
Catalyst composition, wt. %					250°F.		250°F.	
Aluminum	29.8	18.7		5.4	16.2 (16.8)	14.9 (11.4)	15.8 (15.4)	11.4 (0)
Nickel	32.5	30.3		31.7	32.6 (32.3)	29.6 (31.9)	32.6 (31.4)	49.1 (20.1)
Al ₂ O ₃ ·3H ₂ O	37.7	51.0		62.9	51.2 (51.0)	55.5 (52.5)	51.6 (53.2)	39.5 (79.9)
Operating conditions								
Run duration, hr	48	40	300	310	1180	1010	1500	850 ^d
Number of shut downs	75	75	11	150	10	16	19	44
Pressure, p.s.i.g.					150	75	75	122-
Maximum temperature, °F.	760-	770-	775-	800-	690-	750-	720-	160
	835	785	805	885	805	815	830	210
								785-
								875
Feed gas								885
H ₂ /CO ratio	3.7-	3.6-	3.2-	3.0-	2.5-	2.2-	2.5-	2.0-
	4.2	3.8	4.2	3.5	3.7	4.6	3.8	3.4
CO ₂ content, mole %	1	1	0-	0-	0	11-	0-	2.7
						25-	21-	23-
Superficial velocity, ft./sec.	1.0-	1.1-	1.0-	0.5-	0.3	1.0-	0.9-	0.5-
	1.2	1.2	1.2	0.6		1.5	1.7	0.7
Space velocity, SCF/cu.ft. cat.-hr	9,400-	9,700-	9,200-	8,500-	9,200-	9,500-	8,000-	7,400-
	10,800	10,600	11,900	10,400	16,500	13,700	14,800	10,700
				9,700		10,600	12,300	6,400-
Net equivalent methane yield								12,000
lb./lb. nickel					1970	2100	2270	2770 ^d
1000 SCF/lb. alloy					19.9	21.3	22.9	27.9
Catalyst recovery, vol. %					25	45	40	70

- a Double preparation (200 cc. of alloy)
b Based on nominal 58 wt. % aluminum content of alloy.
c Recovered catalyst analyses are given in parenthesis.
d Includes a number of short tests at a variety of operating conditions.

Table 4.-TYPICAL FLUID-BED PILOT UNIT METHANATION TEST RESULTS WITH
RANEY NICKEL CATALYST AND PURIFIED 3:1 H₂/CO RATIO SYNTHESIS GAS

Run No.	0.343 cu.ft. of original alloy			0.5 cu.ft. of catalyst		
	P-7	P-11	P-15	P-19	P-20	P-21
Total steady state duration, hr	6	75	126.5	131.5	19.75	37.75
Pressure, p.s.i.g.	11	143	162	190	110	103
Temperature, °F						
Bottom of Reactor	705	730	810	870	800	860
9 inches from bottom	--	--	--	--	--	805
18 inches from bottom	695	745	815	870	805	825
27 inches from bottom	--	--	--	--	--	830
36 inches from bottom	690	675	735	775	745	730
54 inches from bottom	710	575	630	680	650	--
72 inches from bottom	710	590	640	670	650	--
90 inches from bottom	700	585	640	670	650	--
Downterm inlet temperature, °F.						
Jacket	700	585	635	685	595	605
Bayonets	700	575	640	685	510	605
Feed Gas						
Space velocity, SCF/cu.ft. cat.-hr.	712	3491	3761	5708	5888	5761
Total gas rate, SCF/hr.	244	1193	1287	1977	2031	2881
Gas rate, bottom reactor, %	68	82	79	81	82	89
Gas rate, 12 inches from bottom, %	--	--	--	--	--	11
Gas rate, 18 inches from bottom, %	32	18	21	20	19	--
Superficial bottom inlet velocity ft./sec.	0.35	0.34	0.34	0.47	0.44	0.87
Product gas						
SCF/SCF feed	0.702	0.339	0.312	0.304	0.293	0.282
Carbon recovery, %	100	77	78	102	100	105
Oxygen recovery, %	64	18	13	70	67	67
Composition, mole %						
CO ₂	2.4	7.4	5.8	2.9	4.3	Feed 8.8
H ₂	20.3	24.6	23.3	22.3	23.1	22.0
CH ₄	77.3	20.1	14.0	13.9	26.1	5.4
N ₂	0.2	69.5	77.1	79.8	66.6	73.7
Total	100.0	100.0	100.0	100.0	100.0	100.0
CO ₂ -free specific gravity, air = 1.000	0.445	0.463	0.496	0.500	0.435	0.543
CO ₂ -free heating value, B.t.u./SCF	791	818	863	865	781	916
Water formation, moles/mole feed gas						
By hydrogen balance	0.2618	0.1931	0.2057	0.2287	0.2026	0.2481
By oxygen balance	0.2125	0.2338	0.2378	0.2354	0.2231	0.2217
By condensate measurement	0.2158	0.2315	0.2146	0.2268	0.2127	0.2489
H ₂ -CO conversion, %	85	96	98	97	93	98

^aExcluding water formed by methanation reactions.
^bIncludes small amount of C₂H₆.
^cMay include some CO not distinguishable from N₂ by mass spectrometer analysis when present in small concentrations.

Complete CO conversion was obtained over the entire range of space velocities investigated, and H₂-CO conversions were normally above 90%. Some of the variation in the H₂-CO conversions was the result of small changes in feed gas H₂/CO ratio. The product distribution was very close to equilibrium values^{9,14} calculated on the basis of Reactions (4) and (6), except when catalyst activity limited H₂-CO conversion at high space velocities and relatively low temperatures. Reduction in temperature of approximately 70°F. below the level necessary to maintain equilibrium conversions resulted in a significant increase in H₂ breakthrough, CO₂ formation, and total dry product gas volume, accompanied by a decrease in CH₄ concentration (compare the two test periods reported for Runs P-11 and P-15). The increased amounts of combined oxygen (CO₂) and free hydrogen in the product gas were balanced by decreased water formation. At temperatures high enough to maintain adequate catalyst activity there was little net carbon dioxide formation.

The catalyst bed temperature increase with increases in throughput rate was accompanied by a decrease in Dowtherm inlet temperature from approximately 700°F. to 600°F. This indicates that it was possible to remove the exothermic heat of reaction at the lower space velocities under essentially isothermal conditions, whereas at the high throughput rates a temperature difference of approximately 300°F. between the catalyst bed and the Dowtherm was required. For a heat of reaction of approximately 100,000 B.t.u./pound-mole of methane (equivalent to approximately 65 B.t.u./SCF of H₂ + CO converted), and assuming an actual catalyst bed height of 3 feet equivalent to a heat transfer area of 8.7 sq. ft., the overall heat transfer coefficient between the catalyst bed and the circulating Dowtherm was on the order of 50 B.t.u./hr.-sq. ft.-°F. It is estimated that the overall coefficient for the cooling bayonets was actually on the order of 100 B.t.u./hr.-sq. ft.-°F. because of the lower Dowtherm film resistance at the high flow rates in the bayonets as compared to the jacket.

The test program with the original charge of catalyst was discontinued because of excessive pressure drops through the reactor. Inspection of the reactor offtake section showed that the four 1-1/2 x 9-inch porous stainless steel gas filters were clogged with a considerable quantity of catalyst fines. Since this condition was probably aggravated by the offtake design and inadequate filter area, these equipment components were modified by the addition of a 16-inch diameter x 2-foot section to the disengaging zone. This section housed four 3 x 18-inch porous stainless steel filters with a combined area three times as large as that of the original installation.

In addition, the 1/2-inch Schedule 40 cooling bayonets were enlarged to 3/4-inch Schedule 40 pipe to give an increase of approximately 25% in the cooling surface to catalyst volume ratio (17.0 sq. ft./cu. ft. to 21.4 sq. ft./cu. ft.). The gas inlet system was also enlarged to reduce the high pressure drop encountered at the higher gas rates. It was hoped that these changes would permit attainment of the nominal 3000 SCF/hr. synthesis gas capacity desired for integrated pilot plant operation.

The modified reactor was operated at approximately 100 p.s.i.g. with a catalyst charge consisting of approximately 1/3 recovered catalyst from the preceding test period, and 2/3 of catalyst prepared by the original procedure, which had been stored under water for nearly one year. The total catalyst volume, measured under water, was approximately 0.5 cu. ft. In two runs totalling 44 hours of steady-state operation with H₂/CO ratio synthesis gas produced by reforming of natural gas, feed gas rates ranging from 1400 to 3300 SCF/hr. were investigated. Gases of

about 900 B.t.u./SCF and 84 mole % CH_4 content were produced up to the highest feed rate, confirming that the desired capacity of the reactor could be attained. Typical run data for the modified reactor are given in the last two columns of Table 4. They indicate substantially lower hydrogen breakthrough, and somewhat higher $\text{H}_2\text{-CO}$ conversion, than were obtained with the original catalyst charge and reactor design.

On the basis of these pilot plant test results, it appears that a practical full-scale, dense-phase fluid-bed methanation reactor can be designed for high-capacity, one-pass operation, although such a reactor will have a relatively shallow catalyst bed. For example, at typical operating conditions of 1 ft./sec. superficial feed gas velocity, 5000 SCF/cu.ft. catalyst-hr. feed gas space velocity, 300 p.s.i.g., 750°F. catalyst bed temperature, 550°F. coolant temperature and at a heat transfer coefficient of 100 Btu/hr.-sq.ft.-°F, a 10-foot diameter methanation reactor would require about 2500 1-inch tubes for heat removal, and would contain an unexpanded catalyst bed about 6.6 ft. deep, equivalent to an unexpanded catalyst volume of 360 cu.ft. Such a reactor would handle a synthesis gas rate of about 1.8 million SCF/hr. corresponding to a methane production rate of about 450,000 SCF/hr., or over 10 million SCF/day. Lean-phase fluidization may give more flexibility of operation; each of the two reactors constructed by the M. W. Kellogg Company for SASOL in South Africa reportedly handles 9.5 million SCF/hr. of synthesis gas at 5000 tons/hr. catalyst circulation.¹⁷

INTEGRATED PIPELINE-GAS-FROM-COAL OPERATION

The process steps shown in Figure 5 were investigated in a number of exploratory runs. Although only short on-stream periods were possible because of rapid catalyst failure, the indicated operating conditions and results should be representative of those attainable in steady-state operation. The catalysts used in these runs were prepared before the activation, handling and startup procedures described in the preceding sections had been developed. Catalyst failure appeared to be the result of attrition or disintegration, which caused lifting of the bed into the disengaging and filter zone of the reactor, where severe overheating occurred.

The design and operation of the suspension coal gasifier have been fully described elsewhere.³⁴ However, the use of CO_2 instead of air to pressurize the coal feed tank was a departure from the previous procedure, necessitated by the requirement for a low N_2 content of the synthesis gas when a high-heating-value product gas is desired. Intermediate partially purified synthesis gas storage was provided, since the generating capacity under the preferred operating conditions is 20,000 SCF/hr. for limited on-stream periods, whereas the nominal capacity of the remainder of the plant is 3000 SCF/hr.

One of the major problems of integrated operation investigated in the exploratory pilot plant tests was synthesis gas purification. The use of fixed-bed iron oxide purification (9 lb. Fe_2O_3 /bushel) for bulk H_2S removal, and of separate CO_2 removal from the methanated gas, is probably uneconomical in comparison to hot carbonate, ethanolamine or Rectisol scrubbing of the raw synthesis gas for combined H_2S , CO_2 and partial organic sulfur removal.^{2,12,17,21,29,37} However, the scheme employed here has the advantage of allowing CO_2 to remain in the purified synthesis gas, which is beneficial for two reasons: first, it inhibits hydrogen breakthrough and carbon formation, and second, it provides a diluent as a heat sink for some of the exothermic heat of reaction with-

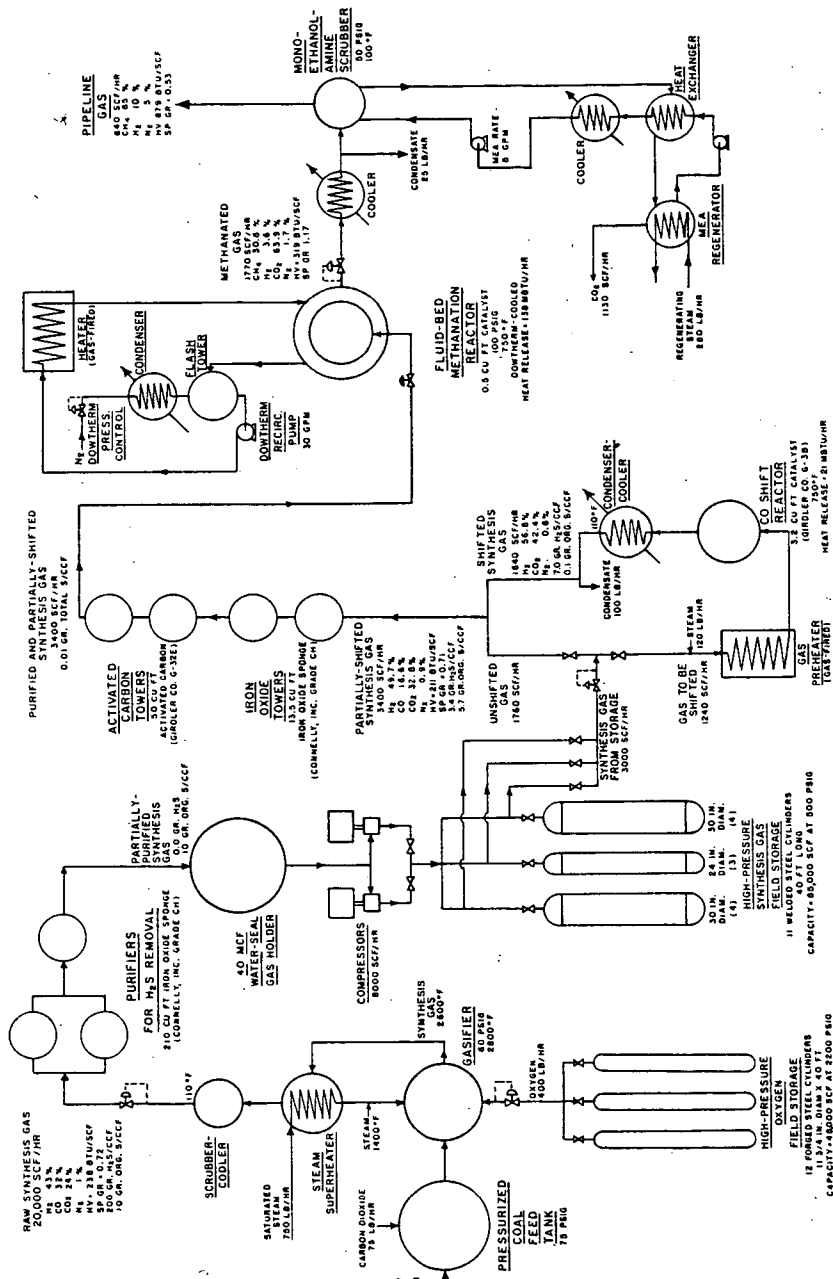


Fig. 5.-SCHEMATIC DIAGRAM OF INTEGRATED PIPELINE-GAS-FROM-COAL PILOT PLANT OPERATION

out the use of gas recycle. Further, in relatively small-scale operation, the highly effective trouble-free and well known iron oxide purification technique appeared preferable from practical considerations.

The organic sulfur (COS and CS_2) concentration of 10 grains/100 SCF used in Figure 5 is only nominal, since it varied considerably with the sulfur content of the coal. In one test with a 4 wt. % sulfur content bituminous coal, the raw gas after bulk H_2S removal contained 26 grains of organic sulfur per 100 SCF; satisfactory operation of the purification system at 3200 SCF/hr. feed rate was still obtained. However, in view of the limited capacity of activated carbon for organic sulfur removal at high partial pressures of CO_2 ,³⁰ it would have been desirable to reduce the load on the carbon towers by the addition of another conventional purification step for selective catalytic conversion of COS and CS_2 to H_2S by hydrolysis and hydrogenation.¹³ With the scheme shown in Figure 5, the synthesis gas bypassing the CO shift reactor had the original organic sulfur content, although the remainder contained only a small amount, since COS and CS_2 conversion proceeds simultaneously with catalytic CO shift. The resulting reappearance of H_2S was easily handled by a second set of small iron oxide towers.

The final CO_2 removal step shown in Figure 5 had not yet been put into operation when the pilot plant program was interrupted to overcome catalyst problems. In practice, it is unlikely that monoethanolamine scrubbing would be competitive with other processes, such as hot carbonate, at the high CO_2 concentrations and pressures involved.^{2,12}

CONCLUSIONS

The technical feasibility of a pipeline-gas-from-coal process utilizing a fluid-bed, partially extracted Raney nickel alloy catalyst for the synthesis gas methanation step was demonstrated. However, rapid mechanical deterioration of this catalyst occurred frequently without a clear indication of the exact causes. This problem was overcome on a laboratory reactor scale by careful control of the caustic leaching step employed for activation of the alloy, by predrying of the catalyst to insure a free-flowing, readily fluidizable charge, and by slow startup in hydrogen. However, successful use of these techniques in the operation of a pilot-plant-scale reactor has yet to be demonstrated. In process variables studies, the use of CO_2 -containing, 3:1 H_2/CO synthesis gases was shown to have a beneficial effect on H_2 - CO conversion to methane under operating conditions where the catalyst activity was sufficient to permit close approach to equilibrium of the CH_4 - CO_2 - H_2O - CO - H_2 system. Organic sulfur tolerance of the catalyst at high contamination levels was approximately 0.5 lb./100 lb. of nickel, indicating the need for purifying synthesis gas to a sulfur content of less than 0.01 grain/100 SCF if active catalyst life is not to be limited below a practical economic level. The total catalyst conversion capacity with purified synthesis gas at 10,000 SCF/cu. ft. catalyst-hr. synthesis gas space velocity, and operating pressures of 75-150 p.s.i.g., was approximately 20,000 SCF of methane/lb. of original Raney alloy, or 2000 lb. of methane/lb. of nickel. This corresponded to an active catalyst life of 1000-1500 hours and an original alloy cost on the order of 5 cents/1000 SCF of methane. Since generally less than half of the catalyst was recovered at the end of a test of this duration, it appears that catalyst life was limited by attrition rather than by deactivation.

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PRODUCTION OF PIPELINE GAS BY HIGH-PRESSURE,
FLUID-BED HYDROGASIFICATION OF CHAR

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Production of high-methane-content (pipeline) gas by direct hydrogenation of coal or low-temperature char^{2,9,14,15} has three major advantages over the two-step partial coal oxidation-synthesis gas methanation process:^{1,13} large reduction, or potential elimination, of oxygen requirements; elimination of the extreme synthesis gas purification requirements prior to catalytic methanation; and greater thermal efficiency through reduction of exothermic heats of reaction. Complete feed utilization will result if less than half of the more reactive coal or char constituents is hydrogasified and the residue is used as a source of hydrogen. However, essentially complete hydrogasification of lignites and some subbituminous coals may be feasible; hydrogen could then be produced by the reforming of a portion of the product gas or the primary natural gas supply.

In earlier phases of this investigation,^{5,14} it was demonstrated in batch reactor tests that gases containing 60-80 volume % methane could be produced by hydrogasification of the lower-rank coals at 1350°F. and 2500-4000 p.s.i.g. By adjustment of hydrogen-coal ratios, gasifications on a moisture-, ash-free (MAF) basis up to 80 wt. % were obtained with bituminous coal, and over 90 wt. % with lignite. However, the residues from bituminous coal hydrogasification were severely agglomerated. As this would hinder smooth operation of a continuous hydrogasification reactor, a pretreatment step yielding nonagglomerating, reactive chars was needed. Optimum reactivity and substantial reduction of agglomeration tendencies of bituminous coal were obtained by fluidized pretreatment in air and nitrogen for about one hour at a maximum temperature of about 600°F; pretreatment with steam as the fluidizing medium did not reduce agglomeration tendencies to the same extent, and pretreatment with carbon dioxide produced chars with the highest agglomeration tendency and also lower reactivity.⁵ Lignite, although essentially nonagglomerating during hydrogasification, was benefited by elimination of CO₂; reactivity was only slightly increased by fluidized pretreatment at about 500°F.⁵

REACTOR DESIGN

After the feasibility of preparing sufficiently reactive, non-agglomerating feeds had been established, a design for a fluid-bed hydrogasification unit was developed. To obtain reliable information on the effects of the process variables, it was deemed necessary to have positive control over bed depth. This required parallel upward flow of pulverized coal or char, and of hydrogen, with discharge through a standpipe. It was felt that if a single-stage cocurrent-flow reactor could not produce gas of the desired heating value, or give hydrogasification yields required for a balanced process, multistage operation could be simulated by a series of operations in a single reactor.

The main design problem was selection of the bed depth, hydrogen superficial velocity and coal feed rate which, at nominal design operating conditions of 1400°F., 1000 p.s.i.g. and 60-325 mesh particle size range, would give a) sufficient agitation for free movement of the bed, b) sufficient gas residence time for utilization of most of the hydrogen feed, and c) hydrogen/coal ratios sufficient for gasification of a substantial portion of the coal feed. Tests were made in glass models of upflow reactors with carbon dioxide at a atmospheric pressure and temperature to simulate the mass velocity of hydrogen at reaction conditions. In a 2-inch diameter reactor with a 1-inch standpipe, adequate fluidization of a 5-foot char bed was obtained at a superficial gas velocity of about 0.06 ft./sec. This corresponded to a gas residence time of 1.3-1.4 seconds and, at a char feed rate of about 4 lb./hr., to a char residence time of 30 minutes and an equivalent hydrogen/char ratio of 20 SCF/lb. It appeared from the batch reactor test results that these conditions should give acceptable gasification results; however, the reactor was designed to accommodate an approximately 9-foot bed for greater operational flexibility.

APPARATUS

The high-pressure semicontinuous coal hydrogasification pilot unit consists of an interconnected pressure vessel assembly that includes a reactor, a char feed hopper, a screw feeder and an ungasified-char-residue receiver (Figure 1). The reactor is designed for a working pressure of 3500 p.s.i.g. at 1500°F. and is fabricated of 19-9 DL alloy. It has an inside effective length of 113 inches, an outside diameter of 5 inches, and an inside diameter of 2 inches. A 1-inch diameter standpipe, of a selected height, provides the reaction annulus, controls the height of the char bed, and serves for the removal of the residual char and product gases from the top of the reactor. Self-sealing closures at the top and bottom of the reactor are of the modified Bridgman type with a stainless steel seal ring.

The char feed hopper is fabricated of Type 316 stainless steel and has an inside diameter of 5 inches, an outside diameter of 6-3/4 inches, and has recently been extended to an inside height of 120 inches. It is fitted with confined gasket-type closures at the top and the bottom. Capacity of the hopper is about 40 pounds of char. In most of the tests reported here, the original hopper with an inside height of 60 inches and half of the present char capacity was used. The hopper is parallel to the reactor and is joined to it by a horizontal feed-screw-housing 24 inches in length (see Figure 2 for details).

The ungasified-char receiver has the same dimensions as the original hopper, and is also fabricated of Type 316 stainless steel. The top of the residue receiver is joined to the bottom of the reactor by a short tube with a self-sealing closure, (modified and full Bridgman, respectively). The residue receiver also acts as a separator for the product gas and the ungasified char. The product gas is passed through a porous stainless steel filter, a water-cooled condenser, and a bank of gas filters for final cleanup. Pressure on the hydrogasification unit is maintained by an externally loaded back-pressure regulator.

Char is transferred through the housing connecting the feed hopper and the reactor by means of a rotating spiral screw with an outside diameter of 5/8 inch, a root diameter of 1/4 inch, and a pitch of 0.40 inch. Delivery of char to the screw within the feed hopper is by gravity. A variable-speed electric motor drive, with belt coupling, rotates the screw. Normal operation is at 25-85 r.p.m. for char rates of 1.5 to 6 lb./hr. Commercial electrolytic hydrogen, recom-

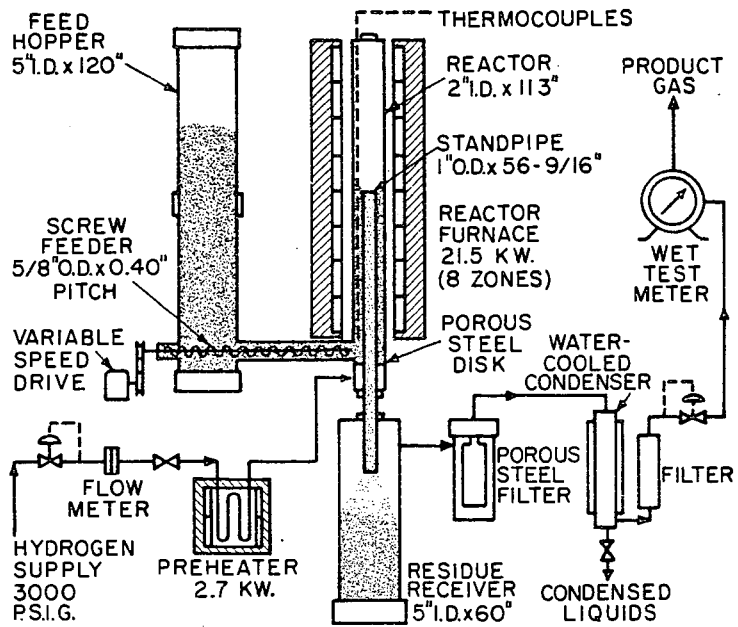


Fig. 1.--COAL HYDROGASIFICATION PILOT UNIT

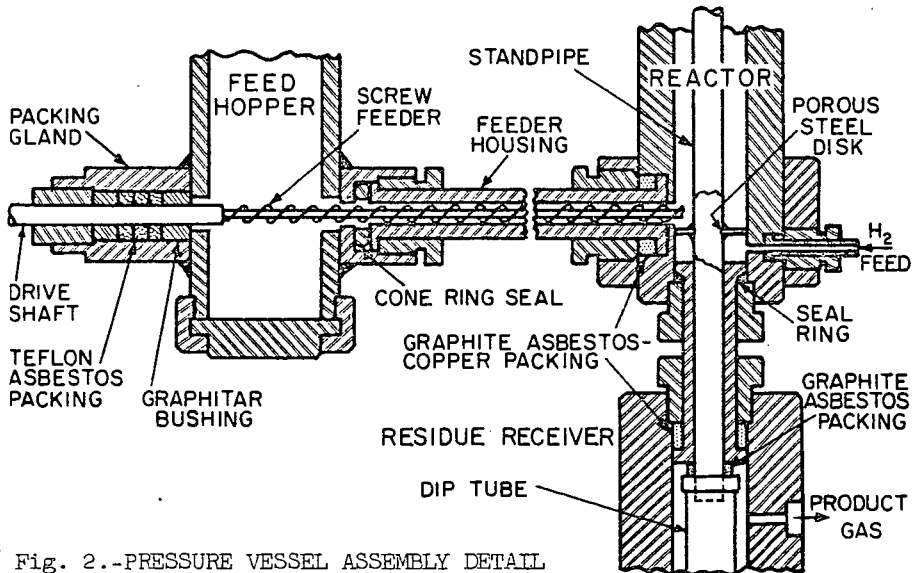


Fig. 2.--PRESSURE VESSEL ASSEMBLY DETAIL

pressed to 3000 p.s.i.g., is fed from a manifolded cylinder bank. A regulator reduces the pressure to a level depending on the desired reactor pressure and hydrogen flow rate. Flow is controlled by a manually operated needle valve, and is metered by a plate orifice with flange pressure taps. Hydrogen enters the reactor preheated to 150°F.

The char bed (reaction) volume is 0.07391 cu.ft. when a nominal 5-foot standpipe (4.714-foot true height) of 1-inch diameter is used. The reactor cross-sectional area, based on a 2-inch by 1-inch annulus, and corrected for two 1/4-inch diameter thermowells that extend the length of the reactor, is 0.01568 sq.ft. A sintered steel disk, of 0.0025-inch mean pore size, which is fastened to the standpipe just below the point where char from the screw feeder enters the reactor, serves as a base for the char bed and as a distributor for the feed hydrogen as it enters the reactor below the disk.

The reactor is heated externally by a 21.5 kw. electric furnace having eight individually controlled heating zones. Char bed temperatures are sensed in ten locations with chromel-alumel thermocouples. Feed hydrogen and gas stream temperatures are also sensed with chromel-alumel thermocouples.

Reactor pressure, differential pressure across the reactor and differential pressure across the hydrogen orifice are continuously recorded. Product gas volume is measured with a wet test meter, and product gas specific gravity is indicated and recorded by a continuous gravitometer.

EXPERIMENTAL PROCEDURE

Feed batches were prepared by crushing and screening the char to a 60-325 mesh size, and drying in air at 110°C. in a forced-convection oven. After the char had been charged to the hopper, the preheated unit was purged with nitrogen and pressurized with hydrogen. The hydrogen orifice meter was then calibrated against the wet test gas meter, the desired hydrogen feed rate established, and the char screw feeder started at a preset rate.

When the char bed reached the top of the standpipe, the differential pressure across the reactor became constant. This differential was normally 20-25 inches of water column, which agreed closely with the value predicted from the bulk density of the expanded char bed; severe fluctuations of differential pressure were an indication of mechanical operating difficulties, such as bypassing of feed hydrogen around the porous steel distributing disk, or plugging of the reactor at the char feed inlet.

The steady-state operating period began when the product gas specific gravity reached a constant value. A composite gas sample was continuously bled into a 10 cu.ft. water-sealed gas holder during the steady-state period; spot gas samples were also taken periodically to confirm other observations relating to attainment of steady operating conditions.

Upon termination of the test, which normally lasted from 4-1/2 to 5-1/2 hours, the unit was depressurized, purged and allowed to cool. Char remaining in the feed hopper, solid residues and condensed liquids were then removed and weighed. Samples of char feed and solid residues were subjected to proximate, ultimate and sieve analyses, and their heating values were determined. Product gases were analyzed with a Consolidated Engineering Co. Model 21-103 mass spectrometer. Carbon monoxide content was determined by infrared

analysis with a Perkin-Elmer Model 12-C infrared spectrometer.

The properties of the composite gas samples, and the char and residue weights corrected to a dry basis, were used in the computation of hydrogasification test results. The char feed rate was computed from the difference between the charged and recovered weights, and from the total feed time. Hydrogen and product gas volumes for the steady-state period were corrected to 60°F. and 30 inches of mercury pressure, and are reported as standard cubic feet (SCF) on a dry basis. Gas heating values and specific gravities were computed from the gas analysis; heating values are reported at 60°F., 30 inches of mercury pressure and saturated with water vapor, whereas specific gravities are for dry gas referred to dry air.

RESULTS

A low-temperature bituminous coal char (Montour No. 10 Mine) supplied by the Research and Development Division of the Consolidation Coal Co. was used in this study. This material was produced in a fluidized carbonization process at much more severe conditions than those employed in the earlier pretreatment study; in batch hydrogasification tests it produced a free-flowing residue, but had significantly less reactivity than chars produced at optimum pretreatment conditions.⁵ It was selected for a study of process variables because of its ready availability and uniform properties, and the prospect of minimum handling difficulties. Unlike the feed material employed in the laboratory semiflow study reported by Hiteshue and others,¹² the char was not impregnated with a catalyst. Typical properties of the feed char and the hydrogasification residues are given in Table 1, and selected results for operation at 500, 1000, 1500 and 2000 p.s.i.g., 1400° and 1500°F. nominal temperature and nominal char feed rates of 2, 4.5 and 6 lb./hr., are given in Table 2. Precise control of char feed rate was not practical; actual values for each feed rate level varied considerably, and the overall range was 1.6-6.3 lb./hr. Normally, hydrogen feed rates corresponded to a superficial velocity of about 0.06 ft./sec., the level required to maintain free flow of char through the reactor; this was equivalent to rates ranging from 34-35 SCF (dry)/hr. at 500 p.s.i.g., to 130-135 SCF (dry)/hr. at 2000 p.s.i.g. Consequently, with the exception of a few tests at a higher hydrogen rate than the minimum, the hydrogen residence time based on the free reaction volume with the 5-foot stand-pipe was nearly constant at 1.2-1.5 minutes.

The average reactor temperatures reported in Table 2 are based on measurements taken 1, 8, 18, 28, 42, and 54 inches above the bottom of the char bed. The closer spacing at the bottom, where temperatures are lowest, is partially responsible for the substantial difference between the average and maximum temperatures; the latter closely approach the nominal temperature levels of 1400° and 1500°F.

The effects of char feed rate and pressure on hydrogasification results at 1400°F. are shown graphically in Figure 3. The char feed rate expressed as space velocity or reciprocal space velocity is used as the independent variable. Char residence times can be computed by assuming a typical bulk density of the expanded bed of 25 lb./cu.ft. The available data for the low-temperature bituminous coal char exhibit the expected trends: increase in the percent of char hydrogasified (on a moisture-, ash-free basis) with increases in pressure and decreases in char space velocity; increase in gaseous hydrocarbon

Table 1.-PROXIMATE, ULTIMATE AND SCREEN ANALYSES
OF CHAR FEEDS AND RESIDUES

Run No.	19		17		45		13		43	
Operating conditions	521		516		1007		1031		1015	
Reactor pressure, p.s.i.g.	1415		1405		1405		1410		1510	
Maximum reactor temperature, °F.	2.07		5.95		1.92		6.26		1.97	
Char feed rate, lb./hr. ^a										
Sample	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue
Proximate analysis, wt. %										
Moisture	0.1	7.1	0.4	4.3	0.0	6.2	0.1	7.0	0.0	6.4
Volatile matter	17.2	3.2	17.1	3.6	17.4	3.8	17.6	4.2	17.1	2.2
Fixed carbon	74.7	79.9	74.4	82.7	75.1	78.7	74.2	79.9	75.3	79.1
Ash	8.0	9.8	8.1	9.4	7.5	11.4	8.1	8.9	7.6	12.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate analysis, wt. % (dry basis)										
Carbon	77.6	83.6	77.4	84.7	78.7	83.9	77.6	84.4	78.1	83.0
Hydrogen	3.15	1.55	3.32	1.82	3.19	1.57	3.30	1.82	3.18	1.28
Sulfur	0.93	0.65	0.93	0.89	0.93	0.76	1.05	0.97	0.93	0.67
Ash	8.0	10.6	8.1	9.8	7.5	12.0	8.1	9.6	7.6	13.2
Nitrogen + oxygen (by difference)	10.32	3.30	10.25	2.79	9.68	1.77	9.87	3.21	10.19	1.85
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating value, B.t.u./lb. (dry basis)	12,877	13,035	12,765	13,214	12,889	12,839	12,133	12,256	12,743	12,584
Screen analysis, wt. % ^b										
+ 40 mesh	0.0	0.0	0.0	0.0	0.1	0.4	0.0	0.0	0.2	0.2
+ 60 mesh	0.0	0.4	0.0	0.2	0.4	0.2	0.2	0.0	0.2	0.4
+ 80 mesh	5.2	1.2	7.2	2.4	10.1	2.2	2.8	1.2	9.4	1.0
+100 mesh	22.0	17.8	21.6	19.6	10.6	7.6	14.2	10.2	12.6	5.6
+140 mesh	10.0	11.2	3.4	8.2	18.4	15.4	9.2	8.6	18.6	14.6
+200 mesh	33.0	33.0	34.6	28.8	23.8	20.0	31.6	32.0	22.2	20.0
+325 mesh	20.6	26.0	19.2	27.6	27.2	29.6	24.4	35.0	25.7	31.8
+325 mesh	9.2	10.4	5.0	14.2	9.4	28.6	17.6	17.0	11.1	26.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Run No.	44		28		31		40		32	
Operating conditions	1001		1518		1512		2012		2004	
Reactor pressure, p.s.i.g.	1505		1405		1435		1425		1415	
Maximum reactor temperature, °F.	6.08		1.76		5.27		2.03		5.75	
Char feed rate, lb./hr. ^a										
Sample	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue
Proximate analysis, wt. %										
Moisture	0.0	5.5	0.1	11.0	0.1	6.9	0.0	10.0	0.1	5.6
Volatile matter	17.9	2.0	16.8	2.9	17.6	2.8	19.7	4.4	19.7	5.1
Fixed carbon	74.1	82.3	76.4	76.0	73.7	81.7	73.1	74.2	73.0	79.1
Ash	8.0	10.2	6.7	10.1	8.6	8.6	7.2	11.4	7.2	11.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate analysis, wt. % (dry basis)										
Carbon	78.4	85.5	78.8	83.1	78.8	85.6	78.5	82.7	78.5	83.4
Hydrogen	3.19	1.25	3.16	1.60	3.16	1.68	3.22	1.73	3.22	2.20
Sulfur	0.95	0.67	1.06	1.27	0.98	1.13	0.93	0.78	0.93	0.93
Ash	8.0	10.8	6.7	11.3	6.6	9.2	7.2	12.7	7.2	11.9
Nitrogen + oxygen (by difference)	9.56	1.78	10.28	2.73	10.46	2.39	10.15	2.09	10.15	1.57
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating value, B.t.u./lb. (dry basis)	12,760	12,966	13,015	12,892	13,032	13,432	13,011	12,432	13,011	13,142
Screen analysis, wt. % ^b										
+ 40 mesh	0.0	0.2	0.0	0.0	0.0	0.9	0.0	0.2	0.2	0.2
+ 60 mesh	0.4	0.2	0.0	0.0	2.0	1.0	1.4	0.2	1.8	1.0
+ 80 mesh	9.2	2.8	24.8	5.2	18.4	7.5	9.0	3.0	13.2	6.3
+100 mesh	11.4	10.4	19.1	11.2	15.0	15.0	12.8	5.8	12.7	12.0
+140 mesh	19.2	20.8	21.0	23.9	20.9	24.9	11.6	13.8	20.0	19.1
+200 mesh	22.0	23.4	20.7	25.7	18.4	22.1	25.2	18.4	21.7	20.9
+325 mesh	26.8	27.3	11.7	19.0	16.2	17.5	32.4	27.3	19.7	21.0
+325 mesh	11.0	14.4	3.7	17.0	9.1	11.1	7.6	35.8	10.7	19.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

a. Based on weight of dry char.
b. U. S. standard sieve series.

Table 2.-OPERATING DATA FOR FLUID-BED HYDROGASIFICATION
OF LOW-TEMPERATURE CHAR AT HIGH PRESSURES

Feed Char: Low-Temperature Bituminous Coal Char, Consolidation Coal Co. Montour No. 10 Mine^a
Particle Size: 60-325 Mesh, U. S. Standard Sieve Series. Char Bed Height: 4.714 ft. Char Bed Volume: 0.07391 cu.ft.

Run No.	19	17	45	11	13	43	22	44	28	25	31	40	41	32
Operating conditions														
Reactor pressure, p.s.i.g.	521	516	1007	1046	1031	1015	1015	1001	1518	1527	1512	2012	2012	2004
Reactor temperatures, °F.														
Maximum	1415	1405	1405	1410	1410	1510	1500	1505	1405	1390	1435	1425	1410	1415
Average	1340	1315	1350	1375	1385	1445	1465	1465	1365	1260	1320	1340	1305	1325
Char rate, lb./hr.	2.07	5.95	1.92	3.59	6.26	1.57	3.68	6.08	1.72	2.93	2.02	4.40	4.40	5.75
Hydrogen rate, SCF/hr.	34.48	34.87	66.50	65.54	66.37	65.50	68.02	69.81	93.15	92.57	102.43	121.45	130.26	132.90
Hydrogen/char ratio, SCF/lb.	16.68	5.86	34.65	18.25	10.60	41.85	18.47	11.19	52.68	24.10	34.13	64.69	29.52	23.12
Char space velocity, lb./cu.ft.-hr.	28.0	80.8	26.0	48.6	84.7	21.2	49.9	82.2	23.8	35.1	27.5	29.5	59.8	77.6
Hydrogen residence time, min.	1.35	1.24	1.33	1.38	1.34	1.29	1.23	1.18	1.49	1.47	1.31	1.34	1.38	1.35
Operating results														
Product gas rate, SCF (dry)/hr.	30.38	27.97	52.82	51.61	54.79	49.50	54.50	51.57	81.28	76.34	77.57	100.36	89.63	92.41
Product gas yield, SCF (dry)/lb.	14.70	6.38	27.52	14.38	8.75	31.63	14.80	8.49	46.14	19.45	14.73	49.39	20.36	16.08
Product gas net B.t.u. recovery, M B.t.u./lb	2.99	1.79	4.53	3.16	2.11	5.19	3.63	2.20	5.46	3.65	3.37	5.62	4.08	3.58
Gaseous hydrocarbon space-time yield, SCF (dry) cu.ft.-hr.	148	199	252	293	335	267	359	380	261	394	505	407	601	669
Net moisture-, ash-free char	26.4	16.3	42.7	29.3	21.1	52.9	32.4	21.3	48.2	32.5	30.3	58.0	40.6	35.5
Carbon gasified, wt. %	23.7	12.1	42.7	28.4	17.7	53.5	30.6	20.9	47.2	32.1	30.5	63.9	43.4	36.2
Feed hydrogen reacted, SCF (dry)/lb.	7.96	2.62	17.62	10.51	6.28	23.89	11.66	8.16	18.57	12.61	12.34	30.74	19.91	16.26
Char residue, lb./lb.	0.687	0.706	0.483	0.650	0.727	0.414	0.699	0.700	0.455	0.609	0.612	0.260	0.501	0.605
Condensed liquid products, lb. B.t.u./lb.	0.0170	0.0031	0.0551	0.0201	0.0174	0.0681	0.0294	0.0395	0.0349	0.0759	0.0381	0.0685	0.0578	0.0445
Residue moisture, lb./lb.	0.0364	0.0264	0.0207	0.0531	0.0500	0.0259	0.0511	0.0364	0.0397	0.0410	0.0378	0.0282	0.0201	0.0326
Material balance, %	98.6	88.8	97.0	98.5	98.8	100.0	107.4	97.5	99.6	102.4	97.5	93.7	96.4	101.1
Product gas properties														
Gas composition, mole %														
N ₂	2.7	4.0	1.5	2.4	2.5	1.6	2.9	0.7	1.2	2.1	1.7	0.7	1.3	2.5
CO	1.9	3.9	1.5	1.5	2.5	1.5	2.1	5.2	0.6	0.6	2.0	0.4	1.3	1.2
CO ₂	1.3	2.9	0.1	0.3	0.4	0.2	0.2	0.5	0.1	0.2	0.1	0.1	0.1	0.2
H ₂	59.2	52.8	61.9	53.9	49.4	56.8	46.1	39.2	74.4	59.0	48.1	68.8	47.6	42.6
CH ₄	37.4	38.4	34.5	39.4	44.7	39.9	48.7	54.2	23.1	37.5	47.7	29.2	48.8	53.1
C ₂ H ₆	0.4	0.4	0.2	0.4	0.5	--	--	0.1	0.5	0.3	0.2	0.6	0.6	0.3
Benzene	0.2	0.2	0.1	0.1	0.2	--	--	0.1	0.1	0.2	0.2	0.2	0.2	0.1
Total	100.6	100.6	100.6	100.6	100.6	100.6	100.6	100.6	100.6	100.6	100.6	100.6	100.6	100.6
Heating value, B.t.u./SCF (a.s.t.)	562	568	560	561	564	594	639	687	482	580	646	530	661	678
Specific gravity, air = 1	0.295	0.370	0.275	0.332	0.374	0.294	0.354	0.396	0.207	0.289	0.343	0.234	0.343	0.369

a. Operating conditions and results based on weight of dry char

b. cu.ft./min. hydrogen at reactor pressure and temperature

c. 100 wt. of product gas - wt. of hydrogen in

d. Hydrocarbons + water

REACTOR TEMP. = 1400°F. BED HEIGHT = 4.7 FT. BED VOL. = 0.074 CU. FT.
 PRESS., P.S.I.G. = $\begin{cases} 500 \\ 34-35 \end{cases}$ $\begin{cases} 500 \\ 64-67 \end{cases}$ $\begin{cases} 1000 \\ 61-67 \end{cases}$ $\begin{cases} 1500 \\ 93-102 \end{cases}$ $\begin{cases} 2000 \\ 130-133 \end{cases}$
 H₂ RATE, SCF/HR. = $\begin{cases} 0.7 \\ 1.3-1.5 \end{cases}$ $\begin{cases} 0.7 \\ 1.3-1.5 \end{cases}$ $\begin{cases} 1.3-1.5 \\ 1.3-1.5 \end{cases}$ $\begin{cases} 1.3-1.5 \\ 1.3-1.5 \end{cases}$ $\begin{cases} 1.3-1.4 \\ 1.3-1.4 \end{cases}$
 H₂ RES. TIME, MIN. = $\begin{cases} 1.3-1.4 \\ 1.3-1.4 \end{cases}$ $\begin{cases} 1.3-1.4 \\ 1.3-1.4 \end{cases}$ $\begin{cases} 1.3-1.4 \\ 1.3-1.4 \end{cases}$ $\begin{cases} 1.3-1.4 \\ 1.3-1.4 \end{cases}$ $\begin{cases} 1.3-1.4 \\ 1.3-1.4 \end{cases}$

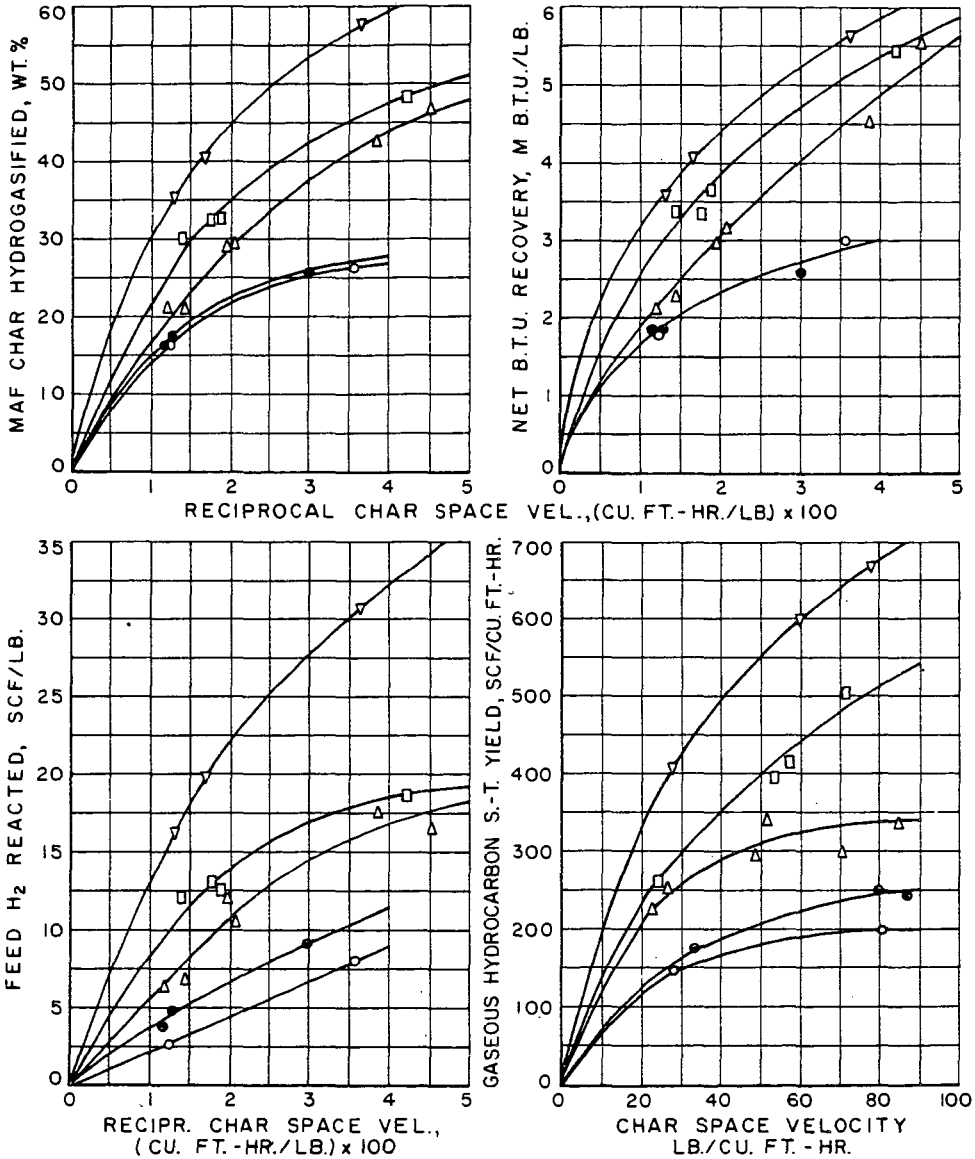


Fig. 3.-FLUID-BED HYDROGASIFICATION RESULTS WITH LOW-TEMPERATURE CHAR

(primarily methane) space-time yield with increases in pressure and increases in char space velocity. The increases in char conversion are accompanied by equivalent increases in the quantity of feed hydrogen reacted - the difference between the amount of hydrogen fed and the amount of unreacted hydrogen contained in the product gas, both per pound of dry char. The net B.t.u. recovery - the difference between the heat of combustion of the product gas and the heat of combustion of the feed hydrogen, both per pound of dry char - also exhibits the same trends as the conversion of char to gas. The data at 500 p.s.i.g. further show that an increase in hydrogen rate to double the level required to maintain a minimum superficial velocity results in a measurable increase in char conversion, gaseous hydrocarbon space-time yield, and quantity of feed hydrogen reacted. Similar results were obtained at higher pressures when the hydrogen feed rate was increased.

The effect of an increase in temperature from 1400° to 1500°F. is indicated in Table 2 in a series of runs at 1000 p.s.i.g. at each of the three feed rate levels. Except for the somewhat erratic behavior of the net B.t.u. recovery, which is an exceedingly sensitive parameter since it is obtained from a relatively small difference of two experimentally determined quantities, this increase in temperature resulted in a small but significant improvement in hydrogasification results.

The char feed and residue analysis data of Table 1 show that, in the course of hydrogasification, the volatile matter and oxygen-plus-nitrogen contents of the char were reduced to a small fraction of the original values, hydrogen content was reduced to about one-half of the original value, and sulfur content remained about the same. The increase in moisture content was caused by water formation through evolution of bound water or reactions of oxygen-containing coal constituents and gasification products with hydrogen; most of this water condensed in the residue receiver and moistened the char residue. Systematic variations of residual char properties with hydrogasification conditions appeared to exist, such as more severe reduction in hydrogen and volatile matter contents at the higher reaction temperature. The screen analyses of the feed and residual chars indicate some size reduction; however, analyses of the residues remaining in the reactor after shutdown showed this was not due to accumulation of larger particles in the reactor.

In the product distributions reported in Table 2, the condensed liquid products consisted primarily of water. Material balances can be seen to be near 100%, and the two parameters of net moisture-, ash-free char hydrogasified and carbon hydrogasified follow similar trends and are of approximately the same magnitude. In conjunction with the consistent behavior of the operating results over the range of test conditions employed, this indicates reliability of the reported data, in spite of the uncertainties introduced by fluid-bed operation at extremely low superficial gas velocities.

DISCUSSION OF RESULTS

The data obtained with low-temperature bituminous coal char and a 5-foot bed height show that a more reactive feed material, a deeper bed, or a number of countercurrent stages will be necessary to achieve both high conversions and high product gas heating values in a single-pass fluid-bed operation. However, an alternate technique for the production of a high-methane-content gas, comprising a hydrogen separation and recycle step, may be more attractive in spite of the

additional process steps required; the gasification rate would be increased by the resulting increase in hydrogen partial pressure, and problems of exothermic heat removal and control of gas-solids contacting greatly simplified. After completion of the present fluid-bed study, moving-bed operation allowing truly countercurrent single-pass contacting may also have to be considered.

Of considerable practical significance are the unexpectedly high gaseous hydrocarbon space-time yields obtained with the bituminous char at 1400°F. A series of studies by Gorin and others^{10,11,16,17} of the kinetics of Disco char gasification with H₂-steam mixtures and pure H₂ in a fluid-bed batch reactor at pressures up to 30 atmospheres (426 p.s.i.g.) and temperatures of 1500°-1700°F. are of interest in this connection. Direct comparison is not possible, since results are reported as differential gasification rates, i.e., rates corresponding to zero bed weight, which is equivalent to conditions where no equilibrium hindrance or other inhibiting effects of reaction products exist. The integral gasification rates obtained in this study would, therefore, be expected to be lower than equivalent differential rates, although this difference should be relatively small at low conversions. It appears that, due to the lower reactivity of Disco char, differential rates of methane formation extrapolated to the conditions of the present study are substantially lower than the integral rates reported in Table 2. For example, in terms of the units employed by Gorin and others, integral rates of methane formation in the 5-foot fluid bed at 1500°F. and 1000 p.s.i.g. ranged from about 70-100 x 10⁻⁴ lb. moles CH₄/lb. atom C per minute over a range of about 50-20% carbon gasification; this is approximately equivalent to extrapolated differential rates for Disco char and pure hydrogen at 1600°F.

At the relatively low pressures and high temperatures employed in the Disco char gasification study, steam was found to greatly accelerate methane formation, in addition to increasing char gasification by reactions leading to the formation of CO, CO₂ and H₂. However, the effect of steam on methane formation decreased rapidly with increases in pressure. This was confirmed in an exploratory fluid-bed test at 1000 p.s.i.g., 1500°F. and 1.1:1 H₂/steam mole ratio, in which the gaseous hydrocarbon space-time yield was 12% lower than in a test at the same conditions with H₂ feed only; a small increase in the rate of gaseous hydrocarbon formation was indicated by comparison with extrapolated data at the same inlet H₂ partial pressure.

The large increase in gaseous hydrocarbon space-time yield with increases in char feed rate, while the hydrogen rate was held nearly constant at each pressure level (Figure 3), occurred in spite of increased equilibrium hindrance from product methane. Since there was no clearly defined tendency for a shift in the source of the hydrogen contained in the gaseous hydrocarbons, this must have been caused primarily by an increase in average reactivity of the char bed. The quantity of feed hydrogen reacted increased nearly in proportion to the gaseous hydrocarbon formation, and corresponded to 80-100% of the hydrogen contained in the gaseous hydrocarbons over the whole range of operating conditions, except for some tests at 500 p.s.i.g. Conversely, the relatively small change in residual char properties with increases in char feed rate and pressure (Table 1) is consistent with the assumption that the increase in the amount of hydrogen supplied by the char was also roughly proportional to the increase in gaseous hydrocarbon formation.

CONCLUSIONS

The feasibility of producing high-methane-content fuel gas by continuous fluid-bed hydrogenolysis of a low-temperature bituminous coal char was demonstrated. In spite of the relatively low reactivity

of the feed material, it was possible to achieve about 40% conversion in a 5-foot bed at 2000 p.s.i.g. and 1400°F. when producing an approximately 50 mole % methane content gas. At these conditions, the gaseous hydrocarbon (mostly methane) production rate was about 600 SCF (dry)/hr.-cu.ft. bed volume, which is sufficiently high to be of commercial interest. Larger conversions were obtained at pressures as low as 1000 p.s.i.g., but at greatly reduced char space velocities, resulting in lower methane production. No major difficulties were encountered in operation of the fluid-bed reactor at an inlet hydrogen superficial velocity of only 0.06 ft./sec. at 500-2000 p.s.i.g. and 1400°-1500°F. Significant improvements in results are expected with deeper beds and more reactive feed materials.

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PROCESS ANALYSIS OF COAL HYDROGASIFICATION
WITH STEAM AND RECYCLED HYDROGEN

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Processes currently under investigation for the production of pipeline gas when needed comprise 1) direct pressure hydrogenation or hydrogasification of hydrocarbonaceous materials as coal and oil shale and 2) catalytic conversion to methane of synthesis gas from coal gasification. Although the latter is the technically more advanced method for synthesis of high heating value gases, coal hydrogasification is considered the more acceptable process for adoption for three principal reasons 1) achievable large reduction to potential elimination of oxygen requirements 2) elimination of sulfur purification necessity except in product gas, and 3) improvement in thermal efficiency through reduction of exothermic heats of reaction.

The hydrogasification process requires external hydrogen, which, as with the synthesis gas methanation process, is obtained, of course, through steam decomposition. The requisite steam decomposition proceeds either by 1) catalytic or partial-combustion reforming of a portion of the product gas or of the primary natural gas supply preferably in those instances where nearly complete conversion of solid fuels to high Btu gas may be realized, i.e. hydrogasification of lignite, reactive non-caking subbituminous coals and chars, oil shale and tar sands or 2) oxygen-steam gasification of solid fuel residues from incomplete hydrogasification of less reactive coals and coal chars. Generally, pressure hydrogasification will not readily convert much over 50% of the carbonaceous matter of most bituminous coals, and due to thermodynamic and kinetic limitations, product gases contain moderate quantities of unreacted hydrogen.

Since costs chargeable to hydrogen production represent a major portion of the total cost of pipeline gas, a potentially advantageous modification of the coal hydrogasification process comprises 1) methane separation by liquefaction or other suitable means to insure maximum heating value of the product gas 2) recycling of the recovered hydrogen to insure full utilization of the gasifying medium and 3) admission of steam in the reactor hydrogasification zone to promote additional hydrogen formation via steam decomposition from the exothermic heat of the coal hydrogenation reactions, thereby improving the heat balance and further decreasing fuel requirements. To be economically attractive the advantages gained must, of course, outweigh the cost increment of product gas separation.

The key concept of the hydrogen recycle process is gasification of coal by simultaneous reaction with steam and recycled hydrogen at elevated pressure and temperature to achieve as near as possible a thermal balance between exothermic and endothermic reactions and to substantially eliminate external hydrogen requirements. The hydrogen produced internally by this scheme would be supplemented by water-gas shift of the hot product gas with additional steam to convert available carbon monoxide. An evaluation of process feasibility requires a thermodynamic

analysis of the C-H₂-H₂O and C-H₂-H₂O-O₂ systems supplemented with interpretation of available kinetic data.

THERMODYNAMIC ANALYSIS OF COAL GASIFICATION WITH STEAM AND HYDROGEN

I. Definition of the Process

Fig. 1 shows a schematic diagram of the proposed coal gasification process. Recycled hydrogen is assumed at 800°F. through heat exchange with the product gas. Process steam is assumed superheated to 1000°F. from an external source. For fixed-bed operation the solid fuel may be fed at the top of the reactor, and for fluid-bed operation the coal charge may be injected with the hydrogen feed stream. After preliminary cleaning of dust, the raw gas, comprising essentially CH₄, H₂, CO, CO₂ and unreacted steam is passed to catalytic water-gas-shift. The gas, then at approximately 1000°F., is cooled in the hydrogen recycle heat exchanger, scrubbed with water to condense unreacted steam, and purified of CO₂, H₂S and other sulfur bearing gases prior to methane separation by liquefaction. Some arrangement of heat exchangers as shown would be necessary to preserve refrigeration economy in liquefaction. The liquid methane could be vaporized and the cold H₂ reheated by the incoming warm gases. The warm H₂ is recompressed by a booster to complete the recycle circuit.

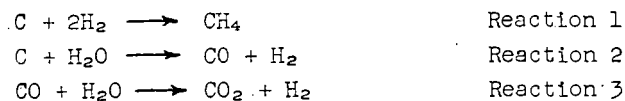
This process may not necessarily require a water-gas shift step, in which event the recycled gas comprises a mixture of hydrogen with moderate amounts of carbon monoxide. Some CO shift would presumably occur in the gasification reactor itself, since moderate excess steam would always be present at the recycle gas introduction point. However, the presence of CO may interfere with the efficient separation of CH₄ by liquefaction. If a water-gas shift reactor is used, then the methane could be separated from the CH₄-H₂ mixture by molecular effusion in "diffusion" cascades, as an alternative to liquefaction.

In the process analysis, which will be directed to operating conditions of the reactor it is assumed that recycled gas consists of hydrogen only. The important variables to be established are temperatures and pressures to make the process thermodynamically feasible. The criteria of feasibility are 1) heat requirements of the reactor per MCF of methane produced, and 2) ratio of hydrogen produced to hydrogen consumed in the process. An analysis of the equilibria and heat effects of the C-H₂-H₂O system is first necessary to establish whether the process can be operated without oxygen as a source of heat through partial combustion.

II. Thermodynamic Analysis of C-H₂-H₂O System

A. Defining Equations

The system is completely defined by the reactions:



The concentrations of the five gaseous components are solved by a procedure of Parent and Katz.⁸ The material balance (Table 1) and relationships are:

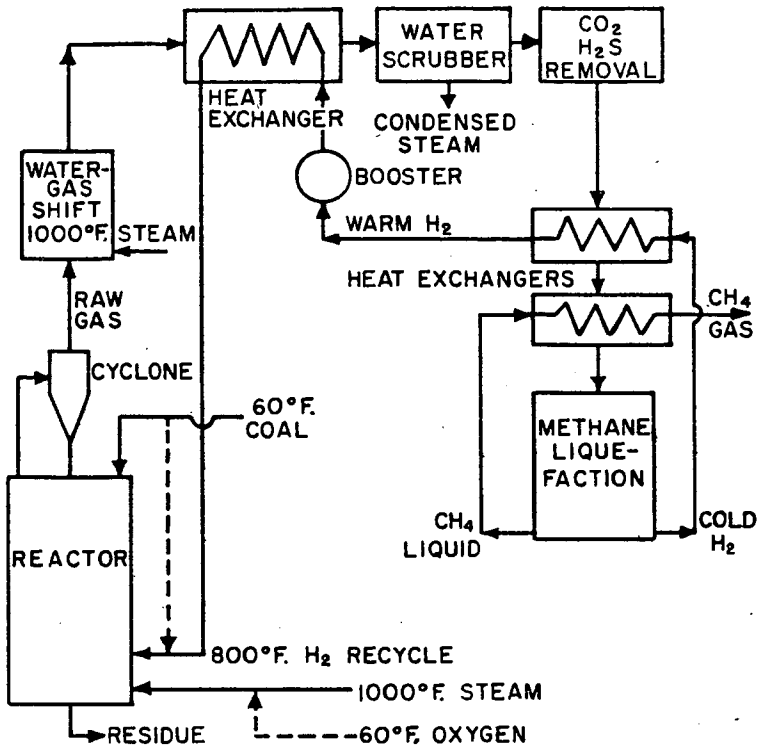


Fig. 1.-SCHEMATIC FLOW DIAGRAM OF
HYDROGEN RECYCLE GASIFICATION PROCESS

Table 1.-MATERIAL BALANCE OF THE C-H₂-H₂O SYSTEM

Component	Initial Amount Moles/Mole Inlet Steam	Equilibrium Partial Pressure, Atm.	Equilibrium Molar Quantities, Moles/ Mole Inlet Steam
C	excess	--	--
H ₂	a	X	x
H ₂ O	1.0	Y	y
CO	0	Z	z
CO ₂	0	M	m
CH ₄	0	W	w
Total		P	N

a) Reaction 1. Equilibrium, for ideal gases

$$K_1 = W/\gamma_c X^2 \quad (1)$$

where γ_c = activity of carbon to hydrogenation

b) Reaction 2. Equilibrium, for ideal gases

$$K_2 = ZX/\gamma_c' Y \quad (2)$$

where γ_c' = activity of carbon to steam

c) Reaction 3. Equilibrium, for ideal gases

$$K_3 = XM/ZY \quad (3)$$

d) Hydrogen balance

$$a = x + y + 2w - 1 \quad (4)$$

e) Oxygen balance

$$y + z + 2m = 1 \quad (5)$$

f) Carbon balance

$$c_g = z + m + w = \text{moles carbon gasified per mole inlet steam} \quad (6)$$

g) Total pressure

$$P = X + Y + Z + M + W \quad (7)$$

h) Total moles at equilibrium

$$N = x + y + z + m + w \quad (8)$$

The following solution from Equations 1, 2, 3 and 7 obtains:

a) CH₄ partial pressure, Atm

$$W = K_1 \gamma_c X^2 \quad (9)$$

b) H₂O partial pressure, Atm

$$Y = \frac{X(X+K_2 \gamma_c')}{2K_2K_3 \gamma_c'} \left[-1 + \sqrt{1 + \frac{4K_2K_3 \gamma_c' (P-X-W)}{(X + K_2 \gamma_c')^2}} \right] \quad (10)$$

c) CO partial pressure, Atm

$$Z = K_2 Y \gamma_c' / X \quad (11)$$

d) CO₂ partial pressure, Atm

$$M = P - X - Y - Z - W = K_3YZ/X \quad (12)$$

For selected temperature, total pressure and assumed carbon activity, equilibrium partial pressures are computed successively by assigning arbitrary X values, or hydrogen partial pressure. Molar quantities are found from:

a) multiplication of the oxygen balance (Equation 5) by P/N, yielding:

$$N = P / [Y + Z + 2M] \quad (13)$$

b) law of additive pressures:

$$x = NX/P, y = NY/P, z = NZ/P, m = NM/P, w = NW/P \quad (14)$$

The required H₂/H₂O inlet molar ratio for the system, from Equation 4, must be zero or positive for a valid solution. Equation 6 yields the quantity of carbon gasified, and the gas composition is defined by the molar quantities. The fraction of steam decomposed, SD, is given by:

$$SD = 1 - y \quad (15)$$

One criterion of process feasibility is the ratio, R, of hydrogen produced to hydrogen consumed, taking into account the CO as equivalent to hydrogen,

$$R = \frac{1-y+z}{2w}, \quad \frac{\text{moles H}_2 \text{ available}}{\text{moles H}_2 \text{ consumed}} \quad (16)$$

As a basis for correction of R for actual fuels, experimental data of Channabassappa and Linden on bituminous coal containing about 75 weight % carbon, and 5 weight % hydrogen, (dry basis) indicate that approximately 80% of the coal feed hydrogen content appears as CH₄ and higher hydrocarbons in the product gas.² An approximation of the quantity of hydrogen available from coal for hydrogasification, expressed as moles/mole inlet steam, is therefore taken to be 0.8 r_H C_g/f, where R_H = hydrogen/carbon molar ratio in coal, and f = fraction carbon gasified. With a coal feed containing 75 weight % C and 5 weight % H, and 95% carbon gasification, this becomes (0.8)(0.4)c_g/0.95 = 0.336 c_g. The corrected ratio, R', hydrogen available to hydrogen consumed, may be written for this case:

$$R' = \frac{1-y+z+0.336c_g}{2w} \quad (\text{corrected for coal}) \quad (17)$$

The recycle gasification process will be independent of an external source of hydrogen if R' = 1.0.

The second test of process feasibility is the net heat effect of the system, ΔH_R, in Btu/lb. mole CH₄ produced. This is given by:

$$\Delta H_R = \Delta H_1 + \frac{1}{w} \left[(1-m-y) \Delta H_2 + m \Delta H_3 + C_g \Delta H_C + a \Delta H_{H_2} + \Delta H_{H_2O} \right] \quad (18)$$

where ΔH₁, ΔH₂, ΔH₃ = heat of reaction, in Btu/lb. mole, of Reactions 1, 2 and 3, respectively, with reactants and products at the temperature of the system, and ΔH = enthalpy of reactant, Btu/lb. mole, between inlet and system outlet temperature.

Thermodynamic equilibrium constants and enthalpy data of the Bureau of Standards^{1,2} were used in all calculations.

B. Equilibrium Computations

The range of variables considered for the C-H₂-H₂O system are 50, 100 and 200 atmospheres, and 1000, 1100, 1200 and 1300°K. with 60°F. inlet carbon, 1000°F. inlet steam, and 800°F. recycled hydrogen. The activity of carbon, γ_c , with respect to the carbon-steam Reaction 2 is taken at unity in all cases. Since experimental results on coal hydrogenation have demonstrated that methane concentrations based on β -graphite-hydrogen equilibrium can be exceeded by as much as 10-20%, it is necessary to consider at least two activities of the carbon, i.e., $\gamma_c = 1.0$ and 1.5, with respect to the carbon-hydrogen Reaction 1. The choice of $\gamma_c = 1.5$ results in CH₄ concentrations approximately 20% in excess of β -graphite-hydrogen equilibrium.

Results of the computations, the majority of which were performed on an ALWAC III digital computer, are listed in Table 2; although many more results were obtained than are tabulated there, those presented are selected as representative of conditions for which the ratios: H₂ available/H₂ consumed, are within the range 0.5-1.4. These data can be plotted against H₂/H₂O inlet molar ratio to determine conditions for which R is exactly 1.0, the point at which the process, at equilibrium, would be independent of external hydrogen.

Typical plots over a wide range of H₂/H₂O inlet molar ratios are given in Fig. 2 for 200 atmospheres, $\gamma_c = 1.0$, 1200°K. (1700°F.) and 1300°K. (1880°F.). In these plots the equilibrium gas compositions and heat effects are shown, and two curves for H₂ available/H₂ consumed are included: one for pure carbon and one for coal containing 75 weight % C and 5 weight % H. It can be seen for the conditions 200 atmospheres, 1200°K. (1700°F.), and $\gamma_c = 1.0$ (Fig. 2A), that at a 1.0 ratio of H₂ available/H₂ consumed, with coal as fuel, the process is endothermic by 35,000 Btu/lb. mole CH₄, and that the equilibrium CH₄ content is nearly 30% (wet basis). The endothermicity decreases with increasing H₂/H₂O inlet molar ratio; however, the ratio of H₂ available/H₂ produced also decreases. Thus at extremely high H₂/H₂O inlet molar ratios the process approaches thermal balance, but requires external hydrogen. At low H₂/H₂O inlet molar ratios the process has sufficient hydrogen, but lacks heat. This is as anticipated, since at low H₂/H₂O inlet molar ratios the endothermic steam decomposition reactions predominate because steam is present in large excess, whereas at high H₂/H₂O inlet molar ratios, the exothermic hydrogenation reactions predominate, since hydrogen is present in large excess.

Therefore, the process cannot attain a self-balanced condition from the standpoint of both hydrogen and heat requirements at 200 atmospheres, 1200°K. (1700°F.), with 1000°F. preheated steam and 800°F. preheated hydrogen. The same results are observed at 200 atmospheres, 1300°K. (1880°F.), and $\gamma_c = 1.0$ (Fig. 2B), where, with a 1.0 ratio of H₂ available/H₂ consumed for coal as fuel, the heat requirement is nearly 50,000 Btu/lb. mole CH₄. An examination of all other conditions given in Table 2 shows that process heat requirements are in the range 25,000-100,000 Btu/lb. mole CH₄ at the operating point determined by a 1.0 ratio of H₂ available/H₂ produced. This heat deficiency will always prevail at all possible gasification temperatures.

Alternate methods for supplying the heat requirements are 1) high preheat of reactants, 2) indirect internal heat exchange with a high-temperature heat transfer fluid, or 3) partial combustion of coal with oxygen within the reactor. In view of the large heat deficiency and the need for rapid heat transfer, the third alternative appears most attractive. This automatically provides a high-temperature zone where a portion of the inlet steam is rapidly decomposed, desirable because

Table 2, Part 2.-EQUILIBRIUM CONCENTRATIONS AND HEAT EFFECTS OF THE C-H₂-H₂O SYSTEM

C as β -Graphite, 60°F.; Inlet H₂ at 800°F.; Inlet Steam at 1000°F.; $\gamma_c' = 1.0$

[illegible]

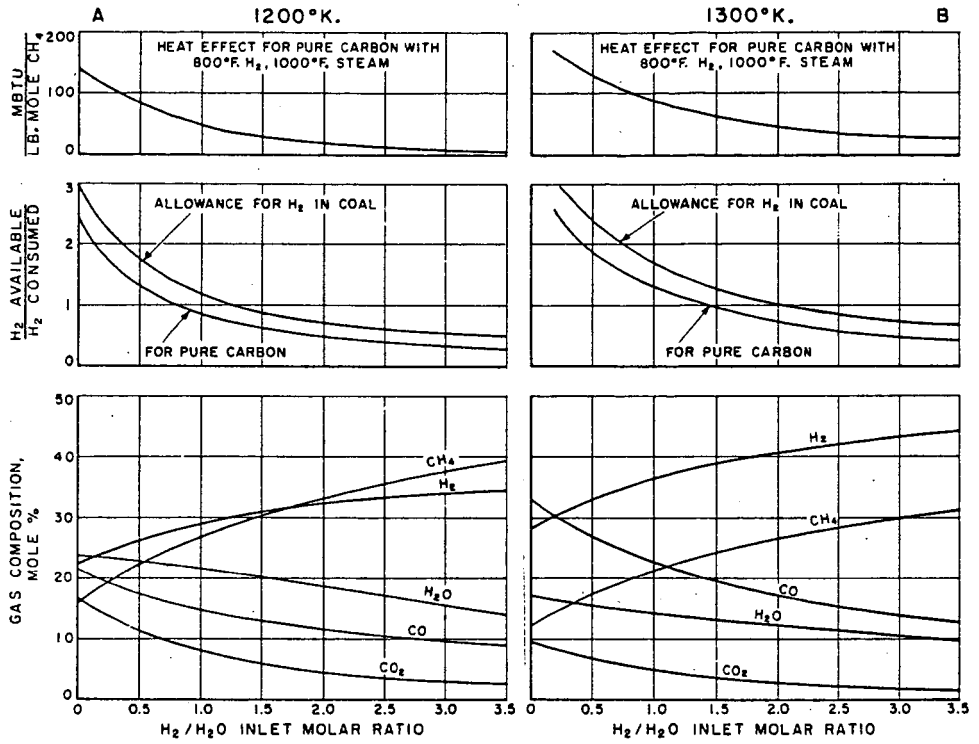


FIG. 2.--EFFECT OF H_2/H_2O RATIO ON EQUILIBRIUM GAS COMPOSITION, H_2 PRODUCTION/CONSUMPTION RATIO, AND NET HEAT EFFECT, FOR THE C- H_2 - H_2O SYSTEM AT 200 ATMOSPHERES AND 1200° AND 1300°K.

steam decomposition rates are relatively slow at the temperatures most favorable to high methane production rates. Since equilibrium steam decompositions cannot be achieved in practice, the C-H₂-H₂O system with oxygen admission is analyzed below on the more realistic basis of equilibrium attained only in the carbon-hydrogen and water-gas-shift reactions, with arbitrary assignment of steam decomposition values.

III. Thermodynamic Analysis of C-H₂-H₂O-O₂ System with Arbitrary Inlet Steam Decomposition.

A. Defining Equations

The system is completely defined by Reactions 1 and 3 in equilibrium, Reaction 2 nonequilibrium, and Reaction 4 to completion:



The method of solution is similar to that given for the C-H₂-H₂O system. The material balance is given in Table 3.

Table 3.-MATERIAL BALANCE OF THE C-H₂-H₂O SYSTEM WITH OXYGEN

Component	Initial Amount Moles/Mole Inlet Steam	Equilibrium Partial Pressure, Atm.	Equilibrium Molar Quantities, Moles/ Mole Inlet Steam
C	excess	--	--
O ₂	b	0	0
H ₂	a	X	x
H ₂ O	1.0	Y	y
CO	0	Z	z
CO ₂	0	M	m
CH ₄	0	W	w
Total		P	N

All previous material balance and equilibrium relationships apply except that Equation 2 is not used, and the new oxygen balance becomes:

$$y + z + 2m = 1 + 2b \quad (19)$$

By manipulation of Equations 1, 3, 7, 15 and 19, the solution for partial pressures and total moles at equilibrium may be written in iterative form:

a) CH₄ partial pressure, Atm.

$$W = K_1 \gamma_c X^2 \quad (9)$$

b) CO partial pressure, Atm.

$$Z = \frac{1}{2} \left[\frac{X(1+d)}{K_3} + 2e \right] \left[1 - \sqrt{1 - \frac{4Xde}{K_3 [X(1+d)/K_3 + 2e]^2}} \right] \quad (20)$$

where $d = \frac{SD + 2b}{1 - SD}$

$$e = P - X - W$$

SD = fraction steam decomposed

c) CO₂ partial pressure, Atm.

$$M = Z / \left[\frac{Xd}{K_3 Z} - 2 \right] \quad (21)$$

d) H₂O partial pressure, Atm.

$$Y = P - X - M - Z - W = XM/K_3 Z \quad (22)$$

e) Total moles at equilibrium/mole inlet steam

$$N = P(1+2b)/(Y + Z + 2M) \quad (23)$$

By assigning arbitrary X (H_2 partial pressure) values, equilibrium concentrations of all other components are computed for a given temperature, pressure, oxygen/steam inlet molar ratio, assumed steam decomposition and assumed activity of the carbon. Gas compositions are computed from Equation 14, and the amount of carbon gasified from Equation 6. The inlet H_2/H_2O molar ratio is determined by Equation 4, for the case of pure carbon as gasification fuel. The ratio may be corrected for hydrogen available from coal as gasification fuel. Under the conditions assumed in the derivation of the previous correction term, the actual H_2/H_2O inlet molar ratio, a' , to the reactor, with coal as fuel, would be:

$$a' = x + y + 2w - 1 - 0.336 c_g \quad (24)$$

One feasibility criterion of the recycle gasification process with oxygen admission is again the ratio H_2 available/ H_2 consumed, Equations 16 and 17. If this ratio is equal to or greater than unity, the process will be independent of an external hydrogen source. By selection of the proper O_2/H_2O inlet molar ratio, the process may be made thermally balanced or slightly exothermic to compensate for heat losses. The net heat effect, Btu/lb mole CH_4 produced, is written in the form:

$$\Delta H_R = \Delta H_1 + \frac{1}{w} \left[(1 - m - y) \Delta H_2 + m \Delta H_3 + b \Delta H_4 + c_g \Delta H_c + a \Delta H_{H_2} + b \Delta H_{O_2} + \Delta H_{H_2O} \right] \quad (25)$$

where ΔH_1 , ΔH_2 , ΔH_3 and ΔH_4 = heat of the respective reactions, in Btu/lb mole, with reactants and products at the temperature of the system, and ΔH = enthalpy of reactant, Btu/lb. mole, between inlet and system outlet temperatures.

An additional calculation for judging the potential efficiency of the gasification process comprises estimation of reactant requirements per MCF CH_4 produced:

$$a) \text{ Lb. steam (reactor only) } = 47.5/w \quad (26)$$

$$b) \text{ Lb. carbon } = 31.7 c_g/w \quad (27)$$

$$c) \text{ Lb. coal (75\% C, 5\% H, at 95\% carbon gasification) } = 44.5 c_g/w \quad (28)$$

$$d) \text{ SCF Oxygen } = 1000 b/w \quad (29)$$

$$e) \text{ Fraction carbon gasified to } CH_4 = w/c_g \quad (30)$$

B. Equilibrium Computations

A limited number of calculations were made at conditions believed favorable for the practical operation of the proposed process. The choice of conditions is based on:

- Inlet steam decompositions in the range 30-50%, comparable to those achieved in oxygen-steam gasification of pulverized coal,^{9,11} or in oxygen-steam fired fixed-bed gasification processes.^{1,13}
- Experimental data on the hydrogenation of coal char in the presence of steam indicate that methane formation rates are too slow to be of commercial interest at pressures below 30 atmospheres and temperatures much below 1200°K. (1700°F.).¹⁵ Hydrogenation rates increase moderately with pressure and rapidly with temperature. However, temperatures above 1200°K. are thermodynamically unfavorable for high methane content of the product gases, despite the increased

hydrogenation rates. Favorable operating conditions appear to be 1200°K. (1700°F.) and 30-50 atmospheres. An increase to 200 atmospheres would permit lower operating temperatures of the hydrogenation zone, perhaps 1000-1100°K. (1340-1520°F.), to take advantage of the more favorable thermodynamic conditions without significantly affecting the hydrogenation reaction rates.

Results of the equilibrium computations and heat effects at 50 and 200 atmospheres, 1200°K. (1700°F.) and 1.0 activity of carbon, are given in Figs. 3 and 4 for 30-40% steam decomposition and 0.1-0.15 O₂/H₂O inlet molar ratio. All data are plotted against H₂/H₂O inlet molar ratio based on pure carbon as fuel. If desired, a correction may be applied for H₂/H₂O inlet molar ratios based on coal as fuel (Equation 24). The plots show general trends:

- a) The ratio H₂ available/H₂ consumed decreases from values greater than 1.0 at low H₂/H₂O inlet molar ratios to values less than 1.0 at high H₂/H₂O inlet molar ratio.
- b) Equilibrium CH₄ contents increase with H₂/H₂O inlet molar ratios.
- c) At the chosen O₂/H₂O inlet molar ratios, the net heat effect, ΔH_R Btu per lb. mole CH₄, is highly negative (exothermic) at low H₂/H₂O inlet molar ratios, and becomes less negative at high H₂/H₂O inlet molar ratios.

The explanation of the trend of the ΔH_R curve lies in the fact that both the O₂/H₂O inlet molar ratio and total inlet steam decomposition were fixed at arbitrary values in these calculations. Under the conditions assumed, the heat available from oxidation is always somewhat greater than that required to decompose the given amount of steam. At a low H₂/H₂O inlet molar ratio to the gasifier, the quantity of methane formed is small. As a consequence the net heat effect per mole CH₄ produced is highly negative (exothermic). At higher H₂/H₂O inlet molar ratios, the quantity of methane increases and more sensible heat is required to bring the reactants to the operating temperature, resulting in a less exothermic heat effect per mole CH₄ produced.

In Fig. 3A for 30% steam decomposition, 0.1 O₂/H₂O inlet molar ratio, 50 atmospheres and 1200°K. (1700°F.), the gasification process becomes independent of external hydrogen if the H₂/H₂O inlet molar ratio is no greater than 1.8, the point at which the ratio H₂ available/H₂ consumed (corrected for coal) approaches unity. At this point, 1) the net heat effect is practically zero with 800°F. preheated recycled hydrogen, 1000°F. steam and 60°F. coal and oxygen, and 2) equilibrium methane content of the wet gas is approximately 15% (21% dry basis). The process would require H₂ recycle in the ratio 3.5 moles/mole CH₄.

In Fig. 3B, for 40% steam decomposition, 0.15 O₂/H₂O inlet molar ratio, 50 atmospheres and 1200°K. (1700°F.), the process would be independent of external hydrogen if the H₂/H₂O inlet molar ratio were no greater than 2.5, the point at which the corrected ratio, for coal, of H₂ available/H₂ consumed approaches unity. In this case the net heat effect is again practically zero for the same reactant preheats, and the equilibrium methane content of the wet gas is approximately 18% (22% dry basis). Under these conditions, the required H₂ recycle is 3.4 moles/mole CH₄ produced.

In Fig. 4A, 30% steam decomposition, 0.1 O₂/H₂O inlet molar ratio, 200 atmospheres and 1200°K. (1700°F.), the process would be hydrogen self-sufficient at H₂/H₂O inlet molar ratios no greater than 0.75, the point at which the corrected ratio, for coal, of H₂ available/H₂ consumed approaches unity. Here the net heat effect is approximately 20,000 Btu/lb. mole CH₄ exothermic, which would be sufficient to compensate for radiation and convection heat losses. The equilibrium

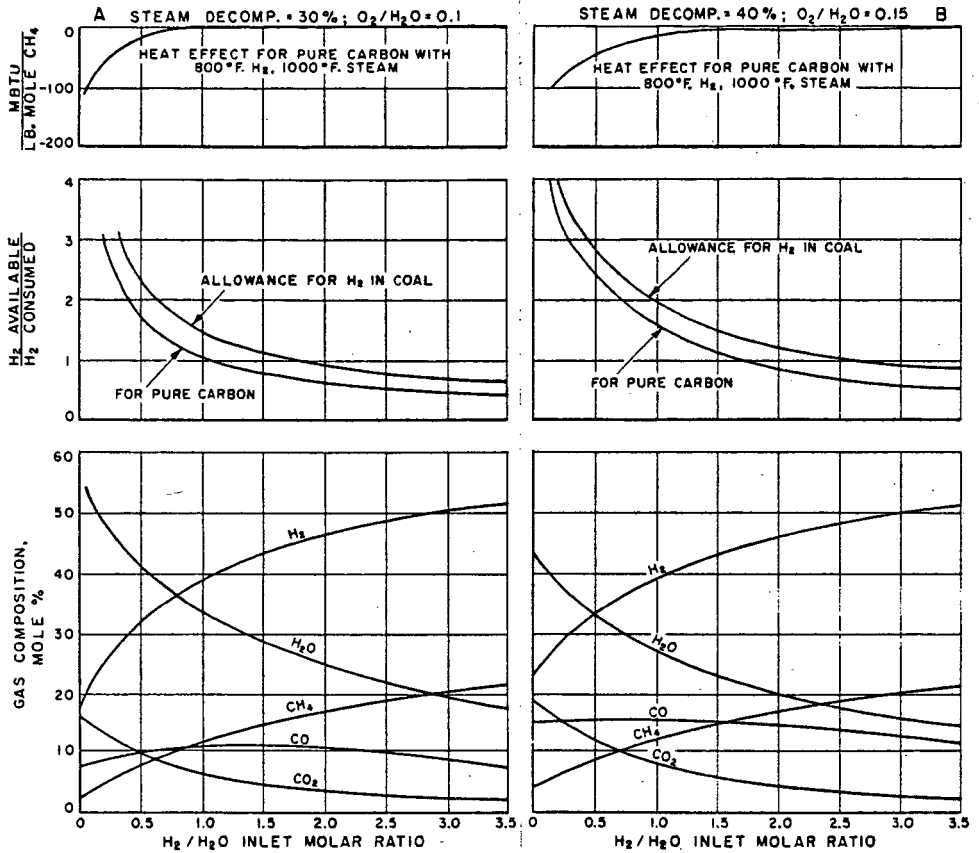


Fig. 3.--EFFECT OF H_2/H_2O RATIO ON EQUILIBRIUM GAS COMPOSITION, H_2 PRODUCTION/CONSUMPTION RATIO, AND NET HEAT EFFECT, FOR THE C- H_2 - H_2O SYSTEM AT 1200°K. AND 50 ATMOSPHERES, WITH 30 AND 40% STEAM DECOMPOSITION, AND 0.1 AND 0.15 O_2/H_2O INLET MOLAR RATIO, RESPECTIVELY

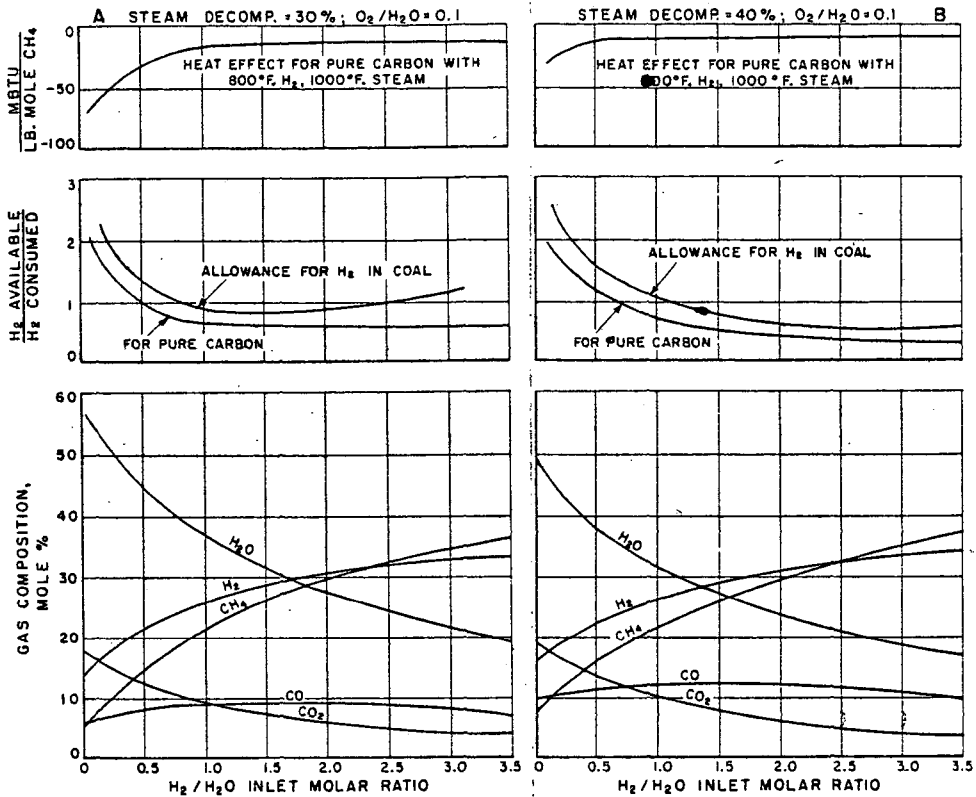


Fig. 4.-EFFECT OF H_2/H_2O RATIO ON EQUILIBRIUM GAS COMPOSITION, H_2 PRODUCTION/CONSUMPTION RATIO, AND NET HEAT EFFECT, FOR THE C- H_2 - H_2O SYSTEM AT 1200°K. AND 200 ATMOSPHERES, WITH 0.1 O_2/H_2O INLET MOLAR RATIO
30 AND 40% STEAM DECOMPOSITION

methane content is approximately 18% on the wet basis, (30% dry basis), and the process would require H_2 recycle of 1.8 moles/mole CH_4 produced.

In Fig. 4B, 40% steam decomposition, 0.1 O_2/H_2 inlet molar ratio, 200 atmospheres and 1200°K. (1700°F.), the process would again be self-sufficient with respect to hydrogen if the H_2/H_2O inlet molar ratio were no greater than 1.0. The net heat effect is less exothermic than in the previous case, approximately 10,000 Btu/lb. mole CH_4 at the same reactant preheats. The equilibrium methane content is approximately 21% on the wet basis, or 31% dry basis, with a required H_2 recycle of 1.7 moles/mole CH_4 produced.

These results demonstrate that operating conditions can be found where the proposed process, with O_2 admission and H_2 recycle, appears thermodynamically feasible. It should be noted, since oxygen is required, that the process reduces to an adaptation of the Lurgi pressure gasifier with provision for H_2 recycle in the upper portions of the fixed fuel bed, or to an adaptation of present fluid-bed coal hydrogenation reactors with provision for addition of steam and oxygen either in the same reactor or in a separate vessel to gasify the coal residue. Since this method of methane production by H_2 recycle takes advantage of the exothermic heat of coal hydrogenation to compensate in part for the endothermic heats of the steam decomposition reactions which continue to occur to a small extent at hydrogenation temperatures, it appears that by virtue of the potentially greater thermal efficiency, both oxygen and coal requirements per MCF CH_4 can be reduced from those of other gasification processes. The potential magnitude of this reduction can be seen from a comparison of the theoretical material requirements in Table 4, based on Figs. 3 and 4, with actual requirements for several gasification processes operated on pilot plant and large scale (Table 5). In Table 4, the oxygen and coal requirements based on Figs. 3A and 3B were increased by 20% to compensate for radiation and convection heat losses, since the theoretical heat effects were not sufficiently exothermic for these two cases.

Table 4.-THEORETICAL MATERIAL REQUIREMENTS (REACTOR ONLY)
FOR METHANE PRODUCTION BY HYDROGEN RECYCLE
AND OXYGEN-STEAM ADMISSION

Reference Figure	Fig. 3A	Fig. 3B	Fig. 4A	Fig. 4B
Conditions:				
Pressure, Atm.	50	50	200	200
Outlet Temp., °F.	1700	1700	1700	1700
O_2/H_2O Inlet Molar Ratio	0.1	0.15	0.1	0.1
H_2/H_2O Inlet Molar Ratio	1.8	2.4	0.75	1.0
Inlet Steam, °F.	1000	1000	1000	1000
Recycled Hydrogen, °F.	800	800	800	800
Inlet Oxygen, °F.	60	60	60	60
Inlet Steam Decomp., %	30	40	30	40
Requirements/MCF CH_4 :				
Pure Carbon, lb.	73.5*	74.5*	64.5	63
Coal, at 95% Gasification, lb.	103*	104*	90.5	88
Steam, lb.	111	79	151	110
Oxygen, 100%, SCF	280*	298*	318	230
Oxygen, 95%, SCF	295*	314*	335	242
Theoretical Percent Carbon Appearing as CH_4	43	43	49	51

* Increased by 20% over theoretical values.

Table 5.-TYPICAL MATERIAL REQUIREMENTS FOR METHANE PRODUCTION FROM SYNTHESIS GAS (COAL GASIFIER ONLY)

Process*	USEM ⁹	PAN ⁴	K-T ¹⁰	IGT ¹¹	L ³	WGS ¹	PROD. ^{1,3}
Nominal Conditions:							
Coal Type	Bit.	Bit.	Bit.	Bit.	Char	Coke	Barley Anth.
Pressure, Atm.	21	1	1	7.5	21	1	1
Outlet Temp., °F.	2500	2350	2300	2500	1100	1200	880
O ₂ /H ₂ O Inlet Molar Ratio	1.5	0.65	0.81	0.45	0.77	0.38	0.29
Inlet Steam, °F.	625	930	250	1500	500	210	285
Inlet Oxygen, °F.	625	930	100	100	500	210	285
Inlet Steam Decompos., %	25	25	25	31	34	54	52
Carbon Gasified, %	90	84	85	92	97	99.5	99.4
Requirements/MCF CH ₄ :							
Carbon, lb.	96.5	119	112	93.5	84	100	87
Coal (or coke), lb.	137	185	168	125	112	111	110
Steam, lb.	42	77	85	131	360	152	154
Oxygen, 100%, SCF	1332	1060	1444	1248	584	1144	951
Oxygen, 95%, SCF	1408	1118	1520	1312	615	1204	1000
Percent Carbon Appearing as CH ₄ by Methanation							
	33	26.7	28	34	38	32	36.6

*PAN = Panindco Process; K-T = Koppers-Totzek Gasifier; L = Lurgi Unit; WGS = Water Gas Set; PROD. = Producer

The data in Table 5 were computed on the basis of 4 SCF CO-plus-H₂ in synthesis gas from coal to yield 1 SCF CH₄ by catalytic methanation. The material requirements pertain only to the coal gasification reactor. Data for Lurgi pressure gasification were adjusted to take into account the methane content of the raw gas.

ESTIMATION OF REACTOR SIZE FROM AVAILABLE DATA ON REACTION RATES

I. Reaction Rate Data

Comprehensive experimental data on reaction rates of hydrogen-steam mixtures with carbon in the form of low temperature (Disco) char have been reported by Gorin, Goring, Zielke and coworkers.^{5,6,14,15} The data were obtained from a 1.5-inch I.D. fluidized bed of 65/100 mesh fuel particles, operated at 1-30 atmospheres and 1500-1700°F. Methane production rates and total carbon gasification rates, expressed as moles C gasified/mole C-min., were determined for pure H₂ and for H₂/H₂O inlet molar ratios in the range 0.1-2.0 at carbon burnoffs or percent gasifications of 0-100%. The total carbon gasification rate is the sum of the rate of CH₄ production and the rate of the steam reactions with carbon. Under the conditions of the investigations, the percent utilization of H₂ and decomposition of steam were small, so the exit gases contained only a few percent CH₄, CO and CO₂. As a consequence, the data do not take into account the retarding effects on the rates as appreciable concentrations of methane and other components appear in the gas in a practical gasification system.

The data reported by Zielke and Gorin¹⁵ indicate that steam has a marked effect in increasing the methane-formation rate; the increase, which is pressure dependent, ranges from 2 to 100 times the rate in a pure H₂ atmosphere, at 1700°F. and 1-30 atmospheres total pressure. The CH₄ rate increases with total pressure raised to a power between 0.1 and 1.5, depending upon H₂/H₂O inlet molar ratio and percent carbon burnoff, and decreases rapidly with decreasing temperature. The total carbon gasification rate follows approximately the same trends, except that at high H₂/H₂O inlet molar ratios this rate becomes equal to the CH₄ rate by virtue of less steam being available for carbon gasification under these conditions. The CH₄ formation rates for Disco char do not appear to be sufficiently high at pressures below 30 atmospheres and temperatures less than 1700°F. to be of particular interest commercially.

To facilitate reactor calculations, plots of data are required showing CH₄ formation and total carbon gasification rates at 50 atmospheres as affected by H₂/H₂O inlet molar ratio and percent carbon burnoff. These graphs were obtained by first plotting the reported rates against pressure (1-30 atmospheres) on logarithmic scales, for each H₂/H₂O inlet molar ratio investigated (0.32, 1.0 and 2.0) at 0-100% carbon burnoff. The resulting nearly straight lines were extrapolated to 50 atmospheres. The extrapolated points were then replotted in the desired form, Fig. 5. The linear CH₄ rate plot, Fig. 5A, was extended (dotted lines) beyond the range of H₂/H₂O inlet molar ratios investigated. The total carbon gasification rate plot, Fig. 5B, was also extended by continuing the trend of the curves (dotted lines) to a 4.0 H₂/H₂O inlet molar ratio. In effect, Figs. 5A and 5B are based entirely upon moderate extrapolations; however, they are believed to be justified.

II. Reactor Design Estimate

A. Procedure

Evaluation, from the standpoint of kinetics, of the hydrogen recycle gasification process with oxygen-steam admission, requires an estimate of the hydrogenation zone fuel bed depth. To avoid unnecessary complications it is assumed that 1) the temperature gradient in the hydrogenation zone of an actual reactor may be approximated with an effective average temperature (1700°F.), and 2) the velocity distribution of gases at a given cross-section of the reactor may be approximated by piston-type flow at an average velocity (constant velocity distribution).

The basic design relationship is given by a material balance⁷ over a differential bed height, dh , in which an incremental quantity of CH₄, dn_m , is formed:

$$dn_m = r_m dh = -q F_o dB \quad (31)$$

where dB = incremental fractional burnup of carbon in the element of fuel bed

dn_m = incremental CH₄ formed, lb. mole/hr.-sq. ft. reactor cross section

r_m = CH₄ formation rate, lb. mole/hr.-cu. ft. reactor

$q = r_m/r_t$ = ratio, CH₄ formation rate/total gasification rate

F_o = carbon input rate to reactor, lb. mole/hr.-sq. ft.

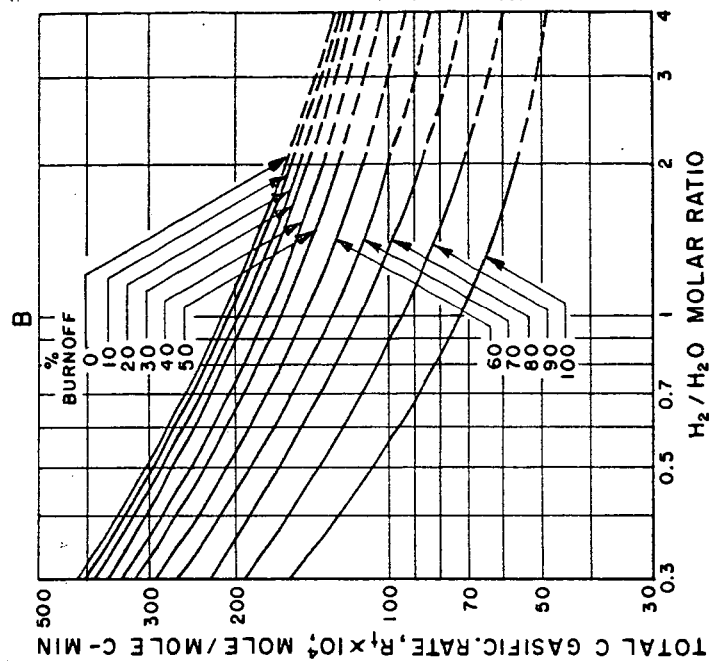
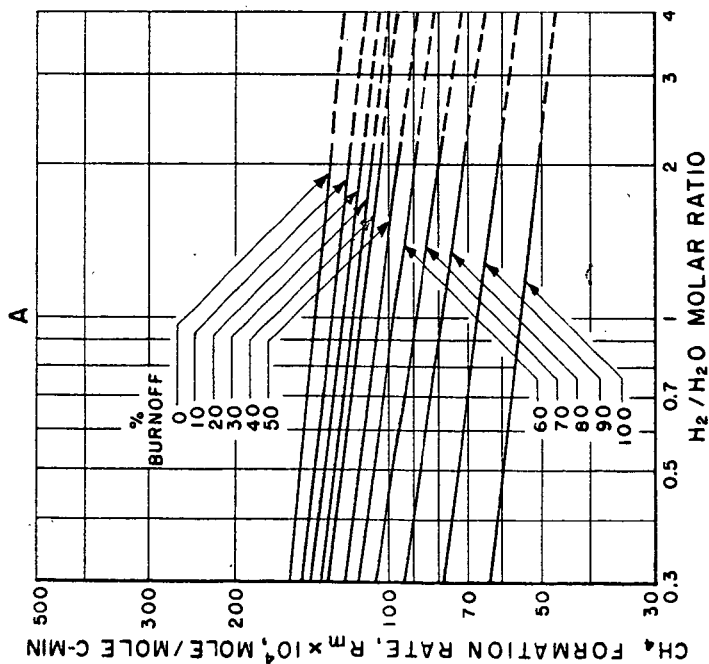


FIG. 5.-METHANE FORMATION AND TOTAL CARBON GASIFICATION RATES FOR DISCO CHAR IN H₂-H₂O ATMOSPHERE AT 1700°F., 50 ATMOSPHERES, AND VARIOUS BURNOFFS OF CARBON

For a fixed fuel bed, with countercurrent flow of gases with respect to the coal feed, this relationship may be integrated graphically over the limits from the start of the hydrogenation zone, $h = 0$, where the burnup is B_0 , to the top of the bed, $h = H$, where the burnup $B = 0$ (fresh coal feed):

$$\int_0^H \frac{dh}{F_0} = \frac{H}{F_0} = - \int_{B_0}^0 \frac{q dB}{r_m} = - \int_{B_0}^0 \frac{dB}{r_t} \quad (32)$$

At a fixed temperature and pressure the quantities r_m , r_t and q are dependent upon carbon burnoff and the composition of the reacting gases. An acceptable relationship to take into account the effect of gas composition in retarding the reaction rates is given by the ratio of the actual partial-pressure product of the reacting components to the equilibrium constant of the particular reaction. By use of this concept, the recommended forms of the rate equations are:

$$R_t' = R_m \left[1 - \frac{P_{CH_4}}{K_1 P_{H_2}^2 \gamma_c} \right] + [R_t - R_m] \left[1 - \frac{P_{CO} P_{H_2}}{K_2 P_{H_2O} \gamma_c'} \right] \quad (33)$$

$$R_m' = R_m \left[1 - \frac{P_{CH_4}}{K_1 P_{H_2}^2 \gamma_c} \right] \quad (34)$$

where R_m = CH_4 formation rate given in Fig. 5A, uncorrected for retarding effects, lb. mole/lb. mole C-min.

R_t = total carbon gasification rate given in Fig. 5B, uncorrected for retarding effects, lb. mole/lb. mole C-min.

R_m' = CH_4 formation rate, corrected for retarding effects, lb. mole/lb. mole C-min.

R_t' = total carbon gasification rate, corrected for retarding effects, lb. mole/lb. mole C-min.

p = actual partial pressure of gaseous components at point of reaction, atm.

γ_c = activity of carbon with respect to hydrogenation reaction

γ_c' = activity of carbon with respect to carbon - steam reaction

These rate equations are considered to give conservative results.¹⁵

The conversion factors between Equations 32-34 are:

$$r_m = 60 \rho_c y_c R_m' / 12 \quad (35)$$

$$r_t = 60 \rho_c y_c R_t' / 12 \quad (36)$$

where ρ_c = bulk density of fuel, lb./cu. ft.

y_c = weight fraction carbon in fuel

For practical purposes the product $\rho_c y_c$ can be considered constant throughout the hydrogenation zone, for fuels of normal ash content. By use of Equation 36, the design Equation 32 may be put in the form:

$$(5 \rho_c y_c) \left[\frac{H}{F_c} \right] = \int_0^{B_0} \frac{dB}{R_t} \quad (37)$$

B. Fixed-Bed Reactor

1. Design Conditions. The integral in Equation 37 is the area under a curve of reciprocal total carbon gasification rate, $1/R_t$, plotted against fractional burnoff, B , in the hydrogenation zone. Since R_t (Equation 33) depends upon the partial pressures of gaseous constituents and upon the burnoff at a given position in the fuel bed, a material balance is required to relate the variation of gas composition with burnoff throughout the fuel bed. The outlet gas composition of the reactor is based on the equilibrium values given in Fig. 3B at the point where the ratio H_2 available/ H_2 consumed (for coal) is unity, for 1200°K. (1700°F.), 50 atmospheres, 40% steam decomposition, 0.15 O_2/H_2O inlet molar ratio, and 2.4 H_2/H_2O inlet molar ratio. This outlet composition is 47.2% H_2 , 17.9% H_2O , 13.5% CO , 3.5% CO_2 and 17.9% CH_4 .

The calculation of gas composition variation with burnoff through the fuel bed is based on, 1) hydrogen, oxygen and carbon balances, 2) 80% of the hydrogen content of the coal released to appear in CH_4 in the hydrogenation zone, weighted linearly according to percent carbon burnoff, and 3) maintenance of water-gas-shift equilibrium. The third assumption is not strictly correct, since experimental evidence indicates that the water-gas shift reaction may be far removed from equilibrium under the operating conditions in coal gasification with H_2 - H_2O mixtures.⁶ However, since the principal discrepancy would lie in the actual CO_2/CO ratio over that theoretically calculated, the assumption of water-gas shift equilibrium will be sufficiently accurate. Final results of the material balances are given in the following.

2. Material Balance for Oxidation Zone. Expressions for the molar quantities of hydrogen (x'), steam (y'), carbon monoxide (z'), carbon dioxide (m'), methane (w'), total moles (N'), and carbon gasified (c_g'), as moles/mole inlet steam are:

$$w' = 0 \text{ (no } CH_4) \quad (38)$$

$$m' = \frac{K_3 (1-SD') (SD' + 2b)}{2K_3 (1-SD') + a' + SD' - 2w'} \quad (39)$$

$$z' = SD' + 2b - 2m' \quad (40)$$

$$y' = 1 - SD' \quad (41)$$

$$x' = K_3 y' z' / m' \quad (42)$$

$$N' = x' + y' + z' + m' + w' \quad (43)$$

$$c_g' = z' + m' + w' \quad (44)$$

Fractional burnoff in oxidation zone:

$$B' = c_g' / c_g \quad (45)$$

where SD' = steam decomposition in oxidation zone:

a' = H_2/H_2O inlet molar ratio corrected for coal. Note $a' = 0$ prior to H_2 recycle point

b = O_2/H_2O inlet molar ratio

c_g = carbon gasified at equilibrium outlet conditions of the hydrogenation zone.

These relationships are readily solved for a given temperature (which determines K_3), known values of a' and b , assumed value of steam decomposition, SD' , and known value of equilibrium carbon gasification, c_g .

3. Material Balance for Hydrogenation Zone. Expressions for the molar quantities of hydrogen (x''), steam (y''), carbon monoxide (z''), carbon dioxide (m''), methane (w''), total moles (N'') and carbon gasified (c_g''), as moles/mole inlet steam are:

$$w'' = \left[\frac{B'' - B'}{B - B'} \right] w \quad (46)$$

$$m'' = \frac{\mu}{2\delta} \left[1 - \sqrt{1 - \frac{4\delta\eta}{\mu^2}} \right] \quad (47)$$

$$z'' = SD'' + 2b - 2m'' \quad (48)$$

$$y'' = 1 - SD'' \quad (49)$$

$$x'' = K_3 y'' z'' / m'' \quad (50)$$

$$N'' = x'' + y'' + z'' + m'' + w'' \quad (51)$$

$$c_g'' = z'' + m'' + w'' \quad (52)$$

Incremental steam decomposition occurring in hydrogenation zone:

$$\Delta SD'' = \left[\frac{B'' - B'}{B - B'} \right] (SD - SD') \quad (53)$$

Total steam decomposition:

$$SD'' = SD' + \Delta SD'' \quad (54)$$

where $\mu = (2K_3 - 1)(1 - SD'') + \delta(SD'' + 2b) + \alpha$

$$\eta = K_3 (SD'' + 2b)(1 - SD'')$$

$$\alpha = a' - \left[\frac{c_g' - w''}{c_g - c_g'} \right] (0.336 c_g) - 2w'' + 1$$

$$\delta = \frac{0.336 c_g}{c_g - c_g'}$$

B = theoretical total burnoff of fuel residue = 100%

B'' = fractional burnoff in hydrogenation zone

SD'' = total steam decomposition in hydrogenation zone

These relationships are solved for a given temperature, assumed reactor inlet and outlet conditions (which determine the values of K_3 , a' , w , c_g , B , SD), and known values of B' , SD' and c_g' (from oxidation zone), by the assigning of arbitrary values to the hydrogenation zone burnoff B'' .

Solution of the material balance equations for the oxidation, steam decomposition, and hydrogenation zones under the condition of exit gas equilibrium resulted in the values given in Table 6. Here the exothermic heat of the oxidation zone is balanced approximately by the endothermic effect of the steam decomposition zone. Beyond the H_2 recycle point, the exothermic heat of coal hydrogenation is

balanced approximately by, 1) the heat requirement of steam decomposition which continues to occur to a small extent in the hydrogenation zone, and 2) the sensible heat required for preheating the coal feed and recycled hydrogen to the operating temperature.

4. Fuel Depth and Flow Rates. The assumption that 10% steam decomposition occurs in the hydrogenation zone (Table 6) can be checked for accuracy after completion of the rate calculations. The results in Table 6 are shown graphically in Fig. 6. The reaction rates of Equations 33 and 34 can now be evaluated at any fractional burnoff and assumed activity of carbon in the hydrogenation zone by reading partial pressure values from this plot and by obtaining the rates R_m and R_c from Figs. 5A and 5B. The results of these calculations, which are required for graphical integration of Equation 37, and later for Equation 31, are summarized in Table 7. The assumption of 1.1 activity of carbon with respect to the hydrogenation reactions is justified on the basis that, given sufficient residence time, the equilibrium CH_4 content based on carbon as β -graphite may be exceeded with carbon as coal.

Table 6.-COMPUTED GAS COMPOSITIONS AT VARIOUS POINTS
IN FIXED BED REACTOR

Basis: O_2/H_2O inlet molar ratio = 0.15;
 H_2/H_2O inlet molar ratio for pure
carbon = 2.41, for coal = 2.01;
coal contains 75 wt. % C, 5 wt. % H.

Position	Assumed Inlet Steam Decomp., %	Theore- tical Carbon Burnoff, %	Gas Comp., Mole %					
			O_2	H_2	H_2O	CO	CO ₂	CH ₄
O_2 - H_2O Inlet to Reactor	0	100	13	--	87	--	--	--
End of Oxidation Zone	0	87.3	--	--	87	--	13	--
End of Steam De- composition Zone	30	58.3	--	21.3	49.8	15.1	13.8	--
Point of H_2 Recycle	30	56.8	--	65.7	19.8	12.0	2.5	--
50% through Hydrogenation Zone	35	28.2	--	56.6	18.8	12.8	3.0	8.8
Outlet of Reactor	40	0	--	47.2	17.9	13.5	3.5	17.9

Molar Quantities, mole/mole inlet steam

Position	Molar Quantities, mole/mole inlet steam							Carbon Gasified
	O_2	H_2	H_2O	CO	CO ₂	CH ₄	Total	
O_2 - H_2O Inlet to Reactor	0.15	--	1.0	--	--	--	1.15	--
End of Oxidation Zone	--	--	1.0	--	0.15	--	1.15	0.150
End of Steam De- composition Zone	--	0.30	0.70	0.21	0.19	--	1.40	0.493
Point of H_2 Recycle	--	2.32	0.70	0.42	0.09	--	3.53	0.511
50% through Hydrogenation Zone	--	1.96	0.65	0.44	0.10	0.303	3.45	0.850
Outlet Reactor	--	1.60	0.60	0.46	0.12	0.605	3.39	1.182

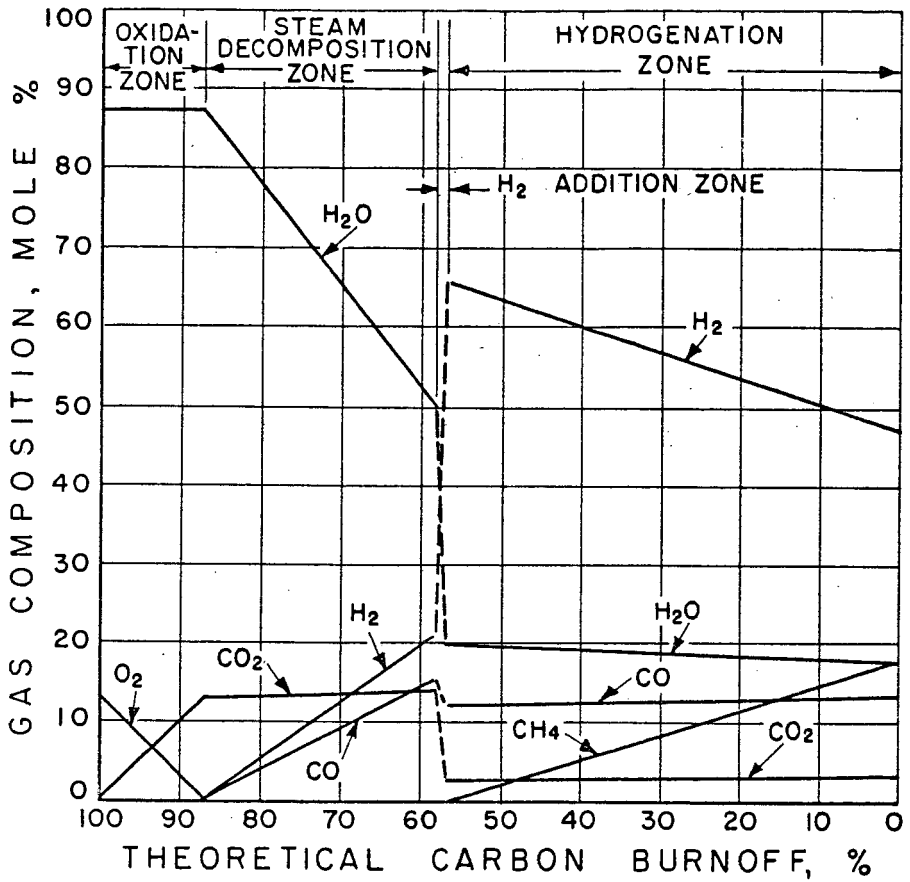


Fig. 6.-COMPUTED VARIATION OF GAS COMPOSITION WITH CARBON BURNOFF IN FIXED-BED REACTOR AT 1700°F. AND 50 ATMOSPHERES.

Table 7.-REACTION RATES FOR VARIOUS PERCENT BURNOFF
IN FIXED-BED REACTOR HYDROGENATION ZONE
OPERATING AT 1700°F. AND 50 ATM.

(Activity of Carbon, $\gamma_c = 1.1$, $\gamma'_c = 1.0$)

Burnoff %	Ratio H_2/H_2O	Inhibiting Terms		Rates, moles/mole C-min.		Ratio $q = R'_m/R'_t$
		$\frac{P_{CH_4}}{K_1 P_{H_2}^2 \gamma_c}$	$\frac{P_{CO} P_{H_2}}{K_2 P_{H_2O} \gamma'_c}$	$R'_m \times 10^4$	$R'_t \times 10^4$	
56.8	3.32	0	0.499	87.0	94.5	0.921
50	3.25	0.06	0.498	85.5	95.1	0.900
40	3.15	0.16	0.492	84.0	93.1	0.902
30	3.04	0.28	0.489	74.1	86.1	0.861
20	2.90	0.45	0.478	60.0	72.0	0.834
10	2.78	0.66	0.462	40.4	52.2	0.774
5	2.71	0.77	0.462	28.1	38.3	0.734
0	2.65	0.91	0.450	11.6	21.0	0.555

From the data in Table 7, graphical integration of Equation 37 yielded a value of 86.25 min.-mole C/mole (inverse space velocity). The probable height of the hydrogenation zone is therefore:

$$H = 86.25 F_0 / 5 \rho_c \gamma_c \quad (55)$$

Practical values of the inlet feed rate F_0 , moles C/hr. sq. ft., can be selected on the basis of a conservative Lurgi rate, 140 lb. coal/hr. sq. ft., and the fact that the incremental burnoff prior to the hydrogenation zone was estimated as 100-56.8, or 43.2% (Table 6):

$$F_0 = (140)(0.75)/(12)(0.432) = 20.2 \text{ moles C/hr.-sq. ft. for a coal containing 75 wt. \% carbon.}$$

Assuming a 40 lb./cu. ft. fuel bed bulk density, the estimated height of the hydrogenation zone is:

$$H = (86.25)(20.2)/(5)(40)(0.75) = 11.6 \text{ ft.}$$

which is applicable only for 65/100 mesh fuel particles. A fixed bed would operate with perhaps 1/4-inch average size fuel. Some correction is therefore required, but necessary data are lacking, for the effect of fuel size, since reaction rates per unit mass of fuel vary with effective surface area and method of contacting.

A verification of the amount of steam decomposition occurring simultaneously with the hydrogenation reactions can now be made, based on the fluid-bed rate data (Figs. 5A, 5B and Table 7), through integration of Equation 31:

$$n_m = -F_0 \int_{B_0}^0 q \, dB \quad (56)$$

and the additional relationship,

$$n_t = -F_0 \int_{B_0}^0 dB = F_0 B_0 \quad (57)$$

where n_m = methane produced in hydrogenation zone, lb. mole/hr.-sq. ft.

n_t = total carbon gasified by hydrogenation and by steam decomposition, lb. mole/hr.-sq. ft.

The incremental steam decomposition occurring in the hydrogenation zone, $\Delta SD''$, is then given by:

$$\Delta SD'' = w (n_t/n_m - 1) \quad (58)$$

where w = methane produced (equilibrium value at outlet of reactor), mole/mole inlet steam. For this case $w = 0.605$ (Table 7), and the ratio $n_t/n_m = 1.19$ (graphical integration), so:

$$\Delta SD'' = 0.605 (1.19 - 1) \text{ or } 11.5\%$$

which is in close agreement with the 10% steam decomposition previously assumed.

Based on these results, the estimated flow rates, space velocities and residence times for the proposed gasification process are:

- a) Steam feed rate, lb./hr. sq. ft., = $18 F_o/c_g = (18)(20.2)/1.182 = 308$
- b) Oxygen feed rate, SCF/hr. sq. ft., = $379 bF_o/c_g = (379)(0.15)(20.2)/1.182 = 970$
- c) Hydrogen recycle space velocity, SCF/hr. cu. ft. hydrogenation zone = $379 a'F_o/Hc_g = (379)(2.014)(20.2)/(11.6)(1.182) = 1125$
- d) Methane space velocity, SCF/hr. cu. ft. hydrogenation zone = $(379) wF_o/Hc_g = (379)(0.605)(20.2)/(11.6)(1.182) = 336$
- e) Approximate coal residence time in hydrogenation zone, hr., based on inlet volume of coal

$$= \frac{H \rho_c y_c}{12 F_o} = \frac{(11.6)(40)(0.75)}{(12)(20.2)} = 1.44$$
- f) Approximate gas residence time in hydrogenation zone, sec., based on average gas volume and 40% void space (ϵ) of the fuel bed

$$= \frac{4940 F_H c_g \epsilon}{N_{avg} F_o T} = \frac{(4940)(50)(11.6)(1.182)(0.40)}{(3.46)(20.2)(2160)} = 9$$

C. Fluid-Bed Reactor

1. Design Conditions. In the analysis of the fluid-bed reactor it is assumed:

- a) The reactor is completely stirred with respect to coal, i.e., the percent carbon burnoff is uniform throughout the hydrogenation zone.
- b) Gases move through the reactor in piston-type flow, i.e., back-mixing is neglected.
- c) The hydrogenation zone is at constant temperature (1700°F.) and constant pressure (50 atm.).
- d) The same equilibrium outlet gas composition will be attained as was assumed for the fixed-bed case calculations.
- e) 30% steam decomposition will be attained prior to the hydrogenation zone. In the hydrogenation zone, an additional 10% steam decomposition will occur.
- f) The water-gas shift reaction is in continual equilibrium in the hydrogenation zone.

g) With the conditions of Items b, e and f above, the gas composition will vary with burnoff as in Fig. 6.

2. Fuel Depth and Flow Rates. By use of the procedure already described, graphical integration of Equation 37 gave 102.9 min.-mole C/mole for the reciprocal total carbon gasification rate (corrected for retarding effects) under the conditions listed above. Details are summarized in Table 8. The probable height of the hydrogenation zone is therefore $H = 102.9 F_0/5 \rho_c \gamma_c$.

Table 8.-REACTION RATES FOR VARIOUS PERCENT BURNOFF
IN FLUID-BED REACTOR HYDROGENATION ZONE
OPERATING AT 1700°F. AND 50 ATM.

(Average Burnoff of Fluid Bed = 56.8%;
Activity of Carbon $\gamma_c = 1.1$, $\gamma'_c = 1.0$)

Burnoff, %	Ratio H ₂ /H ₂ O	Inhibiting Terms		Reaction Rates, mole/mole C-min.		Ratio q = R _m '/R _t '
		P _{CH₄}	P _{CO} P _{H₂}			
		K ₁ P _{H₂} ² γ _c	K ₂ P _{H₂O} γ _c	R _m 'x10 ⁴	R _t 'x10 ⁴	
56.8	3.32	0	0.499	87.0	94.5	0.921
50	3.25	0.06	0.498	80.8	88.8	0.910
40	3.15	0.16	0.492	73.1	81.2	0.901
30	3.04	0.28	0.489	65.0	71.5	0.883
20	2.90	0.45	0.478	48.4	57.8	0.837
10	2.78	0.66	0.462	30.7	40.9	0.752
5	2.71	0.77	0.458	20.5	30.7	0.668
0	2.65	0.91	0.450	8.1	19.1	0.423

The carbon gasification capacity, F_0 , is estimated by assigning a superficial velocity (v_s) of, say, 0.5 ft./sec. at the point of maximum gas flow. The total moles of gases permissible at a chosen pressure, temperature and fluidizing velocity is then $M_L = 4940 P v_s / T$ which with $P = 50$, $T = 2160^\circ R$. becomes $M_L = 34.4$ moles gases/hr.-sq. ft. The total gases are at a maximum at the point of hydrogen recycle. From previous computations (Equations 38 to 45 and Table 6) the ratio of gases at this point is 3.531 moles/mole inlet steam. The total amount of carbon gasified was 1.182 moles/mole inlet steam. Therefore, the carbon input rate is:

$$F_0 = \frac{(1.182)(34.4)}{3.531} = 11.5 \text{ moles C/hr.-sq. ft.}$$

For a fluid bed density of 35 lb. cu. ft. and fuel containing 75 wt. % carbon, the estimated height of the hydrogenation zone is:

$$H = (102.9)(11.5)/(5)(35)(0.75) = 9 \text{ ft.}$$

which again would be applicable only for 65/100 mesh fuel particles.

By use of the procedure of Equations 56-58, the estimated steam decomposition occurring simultaneously with the hydrogenation reactions in the fluid bed is found to be:

$$\Delta SD'' = 0.605 (1.20 - 1) \text{ or } 12.1\%$$

which is in acceptable agreement with the 10% assumption on which the reaction rate calculations were based.

From these results the estimated flow rates, space velocities and residence times for the proposed gasification process are:

- a) Steam feed rate, lb./hr.-sq. ft. = $(18)(11.5)/1.182 = 175$
- b) Oxygen feed rate, SCF/hr.-sq. ft. = $(379)(0.15)(11.5)/1.182 = 555$
- c) Hydrogen recycle space velocity, SCF/hr. cu. ft. hydrogenation zone
= $(379)(2.014)(11.5)/(9)(1.182) = 825$
- d) Methane space velocity, SCF/hr. cu. ft. hydrogenation zone
= $(379)(0.605)(11.5)/(9)(1.182) = 250$
- e) Approximate coal residence time in hydrogenation zone, hr., based
on constant density of fluid bed = $(9)(35)(0.75)/(12)(11.5) = 1.7$
- f) Approximate gas residence time in hydrogenation zone, sec., based
on arithmetic average superficial velocity (\bar{v}_F) of the fluidizing
gases and 60% void space (ϵ) of the fluid-bed = $H\epsilon/\bar{v}_F =$
 $(9)(0.60)/0.294 = 18.4$

These approximate reactor calculations indicate that the hydrogenation zone fuel bed depths for either fixed-bed or a fluid-bed operation are within reasonable values for a practical system. It must be stressed, however, that no interpretation of these results should be made under conditions and assumptions other than those set forth. In particular, the results apply strictly to 65/100 mesh low-temperature coal char made by the Disco process. For lack of experimental reaction rate data at higher pressures, the reported rate data for 1700°F. were extrapolated to 50 atmospheres and were also extended beyond the range of H_2/H_2O inlet molar ratios investigated. The data also apply strictly to a fluid-bed operation, since they were obtained in this type of equipment.

The results derived by application of these rate data to the fixed-bed reactor, although indicative, must be viewed with reservation, since sufficient information is not presently available to correct for possible effects of particle size and of different flow characteristics and gas-contacting efficiencies between fluid-bed vs. fixed-bed operation. For simplicity in the calculations, a constant operating temperature, 1700°F., was assumed throughout the hydrogenation zone. It is possible to improve the results given here by taking into account the expected temperature distribution in the hydrogenation zone through a simultaneous heat balance with the reaction rate calculations.

Further information which is lacking for a more complete evaluation is:

- a) Effect of moderate concentrations of CO and CO_2 in inhibiting the rates of the hydrogenation reactions.
- b) Effect of gasification properties of various fuels, and
- c) Exact costs of methane separation by liquefaction.

SUMMARY AND CONCLUSIONS

Thermodynamic analyses indicate that the proposed process for methane production via coal gasification with recycled hydrogen cannot be independent simultaneously of both external hydrogen and external heat. Operating conditions can be found where, theoretically, either 1) the process is thermally self-sufficient but lacks hydrogen, or 2) the process is self-sufficient with respect to hydrogen, but lacks heat. It is believed that it would be of greater advantage to operate the process according to Item 2 above, since the thermal requirements could be readily met by internal combustion of residual carbon with oxygen. The theoretical heat requirements based on carbon

as β -graphite were found to be in the range 25,000-100,000 Btu/lb. mole CH_4 produced. The heat requirements with coal as the gasification fuel would be still larger, since the exothermic heat of coal hydrogenation is not as large as that for hydrogenation of pure carbon. The use of oxygen for partial combustion would provide, simultaneously, a high-temperature zone for rapid steam decomposition. Decompositions of at least 30% are required for economical utilization of steam, since this is the primary hydrogen source.

Thermodynamic calculations of the revised process, with oxygen admission below the point of hydrogen recycle, show that both thermal and hydrogen self-sufficiency can theoretically be attained at 1700°F. and 50-200 atmospheres. The process is potentially more efficient in respect to the proportion of carbon in the fuel appearing as methane, and represents a method of achieving, theoretically, oxygen requirements less than those of the conventional Lurgi pressure gasifier.

Based on available data on reaction rates of 65/100 mesh low-temperature coal char (Disco) with hydrogen-steam mixtures, fuel bed heights for the hydrogenation zone were estimated at 9 feet for a fluidized-bed reactor, and approximately 11-12 feet for a fixed-bed reactor; at 1700°F., 50 atmospheres, with equilibrium exit gas compositions. These bed heights appear to be within achievable values for a practical gasifier design.

Since the use of oxygen is the preferred method of supplying the heat deficiency, then the proposed process, if operated as a fixed fuel bed, reduces to an adaptation of the Lurgi pressure gasifier modified for hydrogen recycle in the upper portions of the fuel bed. If operated as a fluidized bed, the proposed process with oxygen admission does not differ in principle from fluidized-hydrogenation-residual-fuel-gasification schemes already proposed or already under investigation.

As a single-vessel reactor, the method of methane production by hydrogen recycle would appear to be more effective in a fixed bed by virtue of the countercurrent movement of fuel with respect to the reacting gases. The use of a single-vessel fluid-bed reactor, where both oxygen and hydrogen are introduced, is seen to be of disadvantage by virtue of rapid mixing of fuel, resulting in some volatile matter being burned by oxygen. Since the volatile matter portion of the fuel is the most readily hydrogenated component, it appears that an effective fluid-bed system would require a separate reactor to conduct to completion the volatile-matter hydrogenating reactions, and a second vessel, immediately below the first, to gasify residual carbon with oxygen and steam. The hot gases from the second vessel would be passed directly into the hydrogenation reactor.

From the results of this feasibility study it can be concluded:

- 1) Hydrogen separation by methane liquefaction, coupled with hydrogen recycle, appears to be an attractive approach for pipeline gas production and therefore should be further explored for potential application to present coal hydrogenation methods under laboratory investigation.
- 2) The use of hydrogen recycle to the Lurgi pressure gasifier offers potential improvements in gasification efficiency and oxygen requirement per unit volume of pipeline gas produced.

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